



HAND-BOOK

OF

INORGANIC ANALYSIS;

ONE HUNDRED AND TWENTY-TWO EXAMPLES,

ILLUSTRATING THE MOST IMPORTANT PROCESSES FOR DETERMINING

THE

ELEMENTARY COMPOSITION

OF

MINERAL SUBSTANCES.

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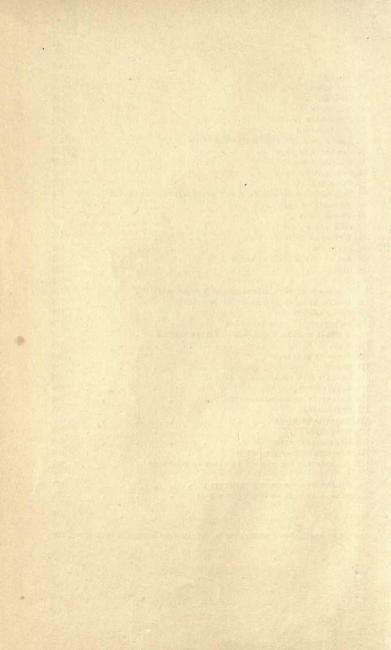
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PREFACE.

This collection of examples for practice in Chemical Analysis, is designed chiefly for the use of the laboratory. It is drawn up under the impression that it is easier for most minds to obtain a clear insight into general relations and laws by the study of special cases, than, inversely, to acquire a knowledge of individual cases by first directing the attention to general rules. An endeavour has been made to arrange the book in such a manner as still to leave enough to demand the reflection of the student and the explanations of the teacher; the latter also must point out the authority for the individual methods here given, if such information should at any time be required.

DR. FRIEDRICH WÖHLER.

The Editor of the English Translation fully concurs with the views which have led the Author to the publication of this volume. General statements, general instructions, will always remain more or less unintelligible to the student, as long as he fails to have a sufficient number of facts at his disposal, by means of which he is enabled to test, in special cases, the correctness of the general rule. The safest plan of construction in Natural Science, will always be found in following the mode in which the truths of Nature have been elaborated, *i. e.*, in proceeding from the study of individual phenomena to the recognition of the law.

The Editor, for many years engaged in laboratory teaching, has often felt the want of a collection of examples similar to that of Professor Wöhler, a translation of which he now offers to the English student. He may state that the English version is nothing more than a faithful representation of the German work, with the exception that the hydrogen scale of equivalents has been substituted for the oxygen scale adopted in the German Edition, and that the formulæ have been written in the symbols generally used in England.

A. W. H.

ROYAL COLLEGE OF CHEMISTRY, NOV. 23, 1853.

HANDBOOK

OF

INORGANIC ANALYSIS.

(QUANTITATIVE.)

1. CHLORIDE OF SODIUM.

NaCl.

Perfectly pure crystallized common salt is strongly heated, to expel adhering moisture, weighed, dissolved in water, the solution slightly acidified with nitric acid, heated, and the chlorine precipitated by nitrate of silver, the liquid being at the same time violently agitated by stirring. When the chloride of silver has completely separated, leaving the liquid clear, it is filtered off and washed (with as little exposure to light as possible), first with hot water acidified with nitric acid, in order that it may not pass through the filter, and subsequently with pure water. When the precipitate has been perfectly dried it is removed as completely as possible from the filter, and fused, in a

weighed porcelain crucible, over the spirit-lamp. The filter is completely incinerated by itself; the ashes are placed upon the cooled chloride of silver, and heated, first with a little nitric acid, in order to oxidize the reduced silver, and afterwards with a few drops of hydrochloric acid; the excess of acid having been expelled, the chloride of silver is again heated to fusion, allowed to cool, and weighed. 100 parts of AgCl contain 24·73 chlorine (and 75·27 silver).

For the determination of the sodium, another weighed portion of chloride of sodium is carefully moistened, in a weighed platinum crucible, with concentrated sulphuric acid; after some time, a gentle heat is applied until all the chlorine has been expelled in the form of hydrochloric acid, when the excess of sulphuric acid is carefully evaporated, and the residual sulphate of soda finally heated to redness, a fragment of carbonate of ammonia being placed in the crucible, to decompose any acid salt. From the weight of the sulphate of soda, that of the sodium is calculated.

2. CHLORIDE OF SILVER.

AgCl.

In order to determine the composition of chloride of silver, a weighed quantity of pure silver is dissolved in dilute nitric acid, the solution precipitated with dilute hydrochloric acid, and the precipitated chloride of silver treated as in No. 1.

Or a weighed portion of fused chloride of silver may be heated with a spirit-lamp, in a bulb-tube, through which a stream of hydrogen is passed until it is completely reduced to metallic silver, which is then weighed.

3. SULPHATE OF SODA. NaO, SO₃ + 10 HO.

For the determination of the water, a weighed quantity of the salt is gradually and carefully heated in a platinum crucible, until the whole of the water is expelled, to ensure which, the heat is finally raised to ignition.

The sulphuric acid is determined by dissolving the salt in water and precipitating with chloride of barium. The liquid is then warmed, and must not be filtered until the sulphate of baryta has completely separated. The clear liquid is then poured upon the filter, without the precipitate, which is stirred up with hot water, again allowed to subside, the clear liquid being poured upon the filter, and the precipitate once more treated in the same way before it is thrown upon the filter, in order that none may pass through the pores of the paper. When perfectly washed, it is dried, separated as much as possible from the filter, the latter being completely incinerated, and its ashes added to the precipitate, which is then ignited and weighed. 100 parts of sulphate of baryta contain 34.29 of sulphuric acid, or 13.71 of sulphur. The amount of soda is determined by difference.

4. TARTRATE OF POTASSA AND SODA.*

Seignette-salt; Rochelle-salt, (KO, NaO, T+8 HO).

The estimation of the water requires the cautious application of heat for a long period. The salt fuses even below

^{*} Prepared by saturating a hot mixture of water and powdered tartar with carbonate of soda, filtering, and crystallizing.

100°, and enters into ebullition at 120°, but does not lose the whole of its water till heated to 215°.

To determine the bases, the salt is ignited, the alkalies dissolved out of the carbonaceous mass by dilute hydrochloric acid, and the filtered solution evaporated to dryness; the mixed chlorides are heated to dull redness in a covered platinum crucible and weighed. They are then dissolved in a little water, and the solution mixed with a moderately concentrated solution of bichloride of platinum. The solution, with the suspended precipitate, is evaporated to dryness on the water-bath, the dry mass digested for some time with alcohol, and the potassio-chloride of platinum collected upon a filter which has been dried at 100°, and weighed. The filtrate, which contains the sodio-chloride of platinum, must still have a distinct yellow colour. The platinum-salt is washed with alcohol, dried at 100°, and weighed. 100 parts correspond to 16.03 of potassium, or 19.33 of potassa.

The amount of the chloride of sodium may be ascertained by deducting the weight of the chloride of potassium from that of the mixed chlorides. It is safer, however, to control this result by direct determination, for which purpose the filtered liquid is carefully evaporated to dryness, and the mass strongly ignited in a covered platinum crucible; in order to ensure the complete decomposition of the chloride of platinum, the ignition should be repeated, with addition of a few crystals of oxalic acid. From the cooled mass, the chloride of sodium is extracted with water.

When, as is frequently the case, the two alkalies are present as sulphates, together with an excess of acid, the greater portion of the latter is expelled by careful evaporation, and the saline mass afterwards ignited in a covered platinum crucible, into which small fragments of carbonate of ammonia are from time to time introduced. The joint weight of the neutral salts thus obtained is then determined.

In order to convert these sulphates into chlorides, the mass is moistened with water, mixed with pure chloride of ammonium, and heated in a covered crucible until the excess of the latter salt is expelled; this operation is repeated until the weight is constant, when the chlorides are separated by means of bichloride of platinum.

Or the solution of the sulphates may be precipitated by a solution of pure acetate of baryta, the precipitate filtered off, the filtrate evaporated to dryness, and the residue ignited. From the carbonized mass, water dissolves the alkalies as carbonates, which are converted into chlorides by treatment with hydrochloric acid.

5. SULPHATE OF SODA AND OXIDE OF AMMONIUM.* NaO, SO₃; NH₄O, SO₃+4 HO.

To determine the amount of soda, a weighed portion of the salt dried at 50° is gradually and carefully heated to redness in a platinum crucible, a fragment of carbonate of ammonia being held in the latter, at the end of the operation, to complete the removal of the excess of sulphuric acid. From the weight of sulphate of soda obtained, that of the soda is calculated.

The sulphuric acid is determined in another weighed portion of the salt, which is dissolved in warm water and

^{*} To prepare this salt, two equal portions of dilute sulphuric acid are taken, the one neutralized with carbonate of soda, then mixed with the other, ammonia added to neutralization, and the solution evaporated to the crystallizing point.

precipitated by chloride of barium. From the weight of the sulphate of baryta, after filtering, washing and igniting, the amount of sulphuric acid is calculated.

The quantity of the ammonia may be estimated according to two different methods.

- a. The weighed salt is dissolved in the smallest possible quantity of water, and the solution mixed with excess of an alcoholic solution of bichloride of platinum, which precipitates the ammonia in the form of ammonio-chloride of platinum. When the precipitate is completely separated, it is filtered off, washed with alcohol, dried, and carefully ignited (see p. 4). From the weight of the residual platinum, that of the oxide of ammonium is calculated. 100 parts of platinum correspond to 26.37 of oxide of ammonium. In order to ascertain that the platinum does not contain any sulphate of soda or chloride of sodium which may have been precipitated by the alcohol, it is washed with water and again weighed.
- b. By distilling the weighed salt with a moderately concentrated solution of soda, the ammonia is evolved, and may be combined with hydrochloric acid. This is best effected in a small flask furnished with a funnel-tube by which the solution of soda is introduced, and a long condensing-tube, the end of which dips into moderately-strong hydrochloric acid. The liquid is retained in ebullition until one-half has distilled over. The hydrochloric solution is carefully evaporated to dryness in a weighed dish, over a water-bath, and the residue of chloride of ammonium weighed; or it may be converted into ammonio-chloride of platinum, which is then treated as above.

After determining the soda, the ammonia and the sulphuric acid, the quantity of the water may be ascertained by difference. It may also be controlled by mixing a weighed portion of the powdered salt, in a platinum crucible, with an excess of freshly-burnt lime, free from water and carbonic acid; the mixture is covered with a layer of lime, the whole weighed, and very strongly ignited over a spiritlamp. The loss of weight represents the joint amount of the ammonia and water.

6. SULPHATE OF POTASSA AND MAGNESIA.*

 KO, SO_3 ; $MgO, SO_3 + 6 HO$.

This salt loses all its water at 133°. The sulphuric acid is determined by precipitation by chloride of barium (see No. 3).

For the estimation of the magnesia, another weighed quantity of the salt is dissolved in water, mixed with chloride of ammonium, subsequently with ammonia, and the magnesia precipitated as phosphate of magnesia-ammonia by adding phosphate of soda. The precipitation is not complete till after the lapse of twelve hours, when the precipitate is collected on a filter and washed with a mixture of 3 parts of water and 1 part of caustic ammonia, in which it is perfectly insoluble. After drying, it is ignited, being thus converted into 2 MgO, PO5 which contains 36.44 per cent of magnesia. The potassa may be determined by difference. If a direct estimation be required, as is frequently the case, especially in the analysis of minerals, the salt is dissolved in water, and the sulphuric acid and magnesia precipitated by a hot saturated solution of hydrate of baryta. The excess of baryta is removed from the filtered liquid by adding a mixture of ammonia and

^{*} This salt is easily obtained in crystals, by mixing a boiling saturated solution of 1 part of sulphate of potassa, with a saturated solution of $1\frac{1}{2}$ part of sulphate of magnesia.

carbonate of ammonia, the filtrate saturated with hydrochloric acid, evaporated, the chloride of potassium feebly ignited and weighed.

If both potassa and soda be present, they are separated as in No. 4.

From the mixed precipitate of magnesia and sulphate of baryta, the former is dissolved by diluted sulphuric acid, and afterwards precipitated and determined as above.

Another method consists in mixing the solution of the double sulphates of magnesia and the alkalies with freshly precipitated carbonate of baryta, and passing washed carbonic acid through the mixture for a considerable time. The sulphate of baryta which is then produced is filtered off, the solution evaporated to dryness, and the mass heated nearly to redness. A mixture of carbonate of baryta, magnesia, and alkaline carbonate is thus obtained, from which the latter may be extracted with water, converted into chloride, and weighed.

7. CARBONATE OF POTASSA AND MAGNESIA.*

 KO, CO_2 ; $2(MgO, CO_2) + 9 HO$.

When ignited, this salt loses \(\frac{3}{4}\) of its carbonic acid, and the whole of its water, leaving a mixture of carbonate of potassa and magnesia, which may be separated by water, and quantitatively determined, the potassa for this purpose being converted into chloride of potassium. The magnesia should not be washed longer than is necessary, since it is not entirely insoluble in water.

^{*} Obtained in crystals on mixing a solution of chloride of magnesium with a saturated solution of bicarbonate of potassa.

The total quantity of carbonic acid contained in the salt is determined by expelling it in an apparatus arranged for the quantitative determination of carbonic acid. The amount of water may then be inferred by difference.

The joint weight of the water and carbonic acid may be determined by fusing a quantity of vitrified borax in a platinum crucible, weighing when cool, introducing the salt, again weighing, and fusing over the spirit-lamp until all the carbonic acid is evolved, and the fused borax becomes clear. The loss of weight expresses the joint amount of water and carbonic acid.

8. EPSOM-SALT AND GLAUBER'S-SALT. MgO, $SO_3 + 7HO$ and NaO, $SO_3 + 10$ HO.

One hundred parts of pure sulphate of magnesia give, by the method described in No. 6, 45.28 parts of phosphate of magnesia. A specimen of Epsom-salt adulterated with Glauber's-salt will give a proportionally smaller quantity of the phosphate. Since 45.28 parts of 2 MgO, PO₅ correspond to 100 parts of crystallized sulphate of magnesia, a specimen of the latter which yields, for example, only 40 parts of 2 MgO, PO₅, would contain only 88.3 per cent of true Epsom-salt, and 11.7 per cent of Glauber's-salt.

In order to test Epsom-salt for Glauber's-salt, the specimen is mixed with powdered charcoal, dried, and heated in a crucible to bright redness. If sulphate of soda be present, water will dissolve out of the cold mass sulphide of sodium, which, when treated with hydrochloric acid, is converted into chloride of sodium, with evolution of sulphuretted hydrogen.

Or the solution of the salt to be tested may be precipi-

tated by hot saturated baryta-water, filtered, the excess of baryta precipitated from the solution by a mixture of ammonia and carbonate of ammonia, and the filtrate evaporated, when, if any Glauber's-salt have been present, carbonate of soda will be left.

9. PHOSPHATE OF SODA AND OXIDE OF AMMONIUM.* NaO, NH₄O, HO, PO₅ + 8 HO.

A weighed quantity of the salt is gradually and cautiously heated in a platinum crucible, the heat being finally raised to ignition, and continued till the salt is in a state of tranquil fusion. The ammonia and water are thus expelled, their joint amount being indicated by the loss of weight. The fused residue is NaO, PO₅.

The determination of the ammonia is effected as in No. 5, with another portion of the salt.

In order to determine the phosphoric acid, the salt is dissolved in water and mixed with chloride of ammonium, ammonia and sulphate of magnesia, the precipitate being treated as in No. 6. The ignited 2 MgO, PO₅ contains 63.55 per cent of phosphoric acid.

For the direct determination of the soda, a weighed quantity of the salt is dissolved in water, and the phosphoric acid precipitated by acetate of lead. From the filtered liquid, the excess of oxide of lead is removed by a mixture of ammonia and carbonate of ammonia, the

^{*} Six parts of crystallized phosphate of soda are dissolved, with the aid of heat, in 2 parts of water, and in this solution 2 parts of chloride of ammonium are dissolved. The filtered liquid deposits crystals of the new salt which are purified by solution in hot ammoniacal water and recrystallization.

solution heated to ebullition, filtered, evaporated to dryness and the residual acetate ignited, with access of air, until the carbonate of soda is colourless.

As a control for the determination of the phosphoric acid, the phosphate of lead may be decomposed by heating with dilute sulphuric acid, and the phosphoric acid precipitated from the filtrate by sulphate of magnesia, as directed above.

10. PHOSPHATE OF MAGNESIA AND OXIDE OF AMMONIUM.*

2 MgO, NH₄O, PO₅ + 12 HO.

By ignition, the salt is converted into 2 MgO, PO₅.

The ammonia is determined by dissolving the salt in the smallest possible quantity of hydrochloric acid, mixing the solution with bichloride of platinum and alcohol, and treating the ammonio-chloride of platinum, as in No. 5.

In order to separate and determine the phosphoric acid and magnesia, the ignited salt is fused in a platinum crucible, over a spirit-lamp, with 4 parts of carbonate of potassa and soda.† The mass is digested with water, the residual magnesia washed, ignited and weighed.

* Prepared by precipitating a solution of sulphate of magnesia to which much chloride of ammonium has been added, by phosphate of soda, and washing the precipitate with dilute ammonia.

† Consisting of equivalent proportions of KO, CO₂ and NaO, CO₂, or 13 parts of the former, and 10 of the latter. Also easily obtained by igniting Seignette-salt free from lime, dissolving, and evaporating to dryness.

The alkaline solution is neutralized with acetic acid, and the phosphoric acid precipitated by acetate of lead. The precipitate is filtered off, washed, dried, detached as far as possible from the filter, which is incinerated in a porcelain crucible, in which the precipitate is then gently ignited and weighed. Since its composition is variable, the quantity of the phosphoric acid cannot be calculated from it. In order to determine this acid, the precipitate is dissolved in warm dilute nitric acid, and the oxide of lead separated by sulphuric acid, alcohol being afterwards added to complete the precipitation.

The sulphate of lead is filtered off, washed, ignited and weighed. From the amount of this precipitate, that of the

phosphoric acid may be calculated.

The phosphate of magnesia and ammonia may also be dissolved in acetic acid, the phosphoric acid precipitated by acetate of lead, the excess of oxide of lead removed from the filtrate by adding a mixture of ammonia and carbonate of ammonia, heating, and filtering. The solution, which contains acetate of magnesia, is evaporated, and the residue ignited, until the magnesia is perfectly white.

Another method of separating phosphoric acid and magnesia consists in dissolving the ignited salt in a little hydrochloric acid, boiling the solution for some time in order to convert the phosphoric acid into the tribasic form, and mixing it, first, with solution of sesquichloride of iron, and afterwards, with excess of acetate of ammonia; if the solution be now boiled for some time, all the phosphoric acid and iron are precipitated, and the magnesia remains in solution. The filtered liquid is evaporated to dryness, the residue heated till all ammoniacal salt is expelled and moistened with sulphuric acid to convert the magnesia

into sulphate. The excess of acid is expelled by heat, and the residual salt gently ignited; from the weight of this residue that of the magnesia, and consequently of the phosphoric acid, is calculated.

11. THE CHLORIDES OF POTASSIUM, SODIUM AND MAGNESIUM.

In the analysis of minerals which are decomposed by hydrochloric acid, there is frequently obtained, after the separation of the other constituents, a mixture of the abovementioned chlorides. The solution, if containing, as is generally the case, ammoniacal salts, is evaporated to dryness, and the mass gently ignited in a platinum crucible until the latter are volatilized. The magnesia and alkalies are then separated according to one of the following methods:

I. The mass is moistened with a concentrated solution of carbonate of ammonia, dried and ignited, during which operation, a fragment of carbonate of ammonia is held within the partially closed crucible. This process is repeated until a constant weight is obtained. A mixture of magnesia and alkaline chlorides is left, from which the latter may be extracted by water. This method is more difficult of execution in proportion as more alkaline chlorides are present.

II. The residue containing the three chlorides is mixed, in a platinum crucible, with some water and a quantity of finely-powdered oxide of mercury; the mixture is digested for some time, dried, and ignited in a covered crucible, when all the chloride of magnesium is decomposed and converted into magnesia.

III. The chlorides are dissolved in a little water, and the solution boiled for a long time with freshly precipitated carbonate of silver, when all the chloride of magnesium is decomposed. The precipitate is filtered off, washed, and the precipitated carbonate of magnesia dissolved out with dilute hydrochloric acid.

IV. The solution of the bases is mixed with some salammoniac and ammonia in excess, and the magnesia precipitated by phosphate of ammonia (see No. 6). From the filtrate the ammonia is expelled by evaporation, and the excess of phosphoric acid precipitated by acetate of lead as a compound of phosphate and chloride of lead. The excess of oxide of lead is precipitated by a mixture of ammonia and carbonate of ammonia; the liquid digested, and the precipitate filtered off. The alkalies are then obtained by evaporation.—This method appears to be the most accurate.

If the three bases are combined with nitric acid, the solution is evaporated, the mass treated, in a platinum crucible, with carbonate of ammonia, and ignited. From the residual mixture of magnesia and alkaline carbonates, the latter are extracted by water.

Should they be in the form of sulphates, the process indicated in No. 4 must be adopted.

12. BITTER-SPAR AND DOLOMITE.

CaO, CO2; MgO, CO2.

The mineral dried at 100° is dissolved in dilute nitric acid, the solution afterwards heated, in order to oxidize any protoxide of iron, and, after cooling, neutralized with am-

monia and rapidly filtered from any precipitate of sesquioxide of iron. The lime is then precipitated by oxalate of ammonia. When the precipitate has subsided, after being digested for some time, it is filtered off, washed, dried and ignited; it is then moistened with carbonate of ammonia, again dried, and gently heated. It is weighed as carbonate of lime. Or it may be moistened with concentrated sulphuric acid, the excess of acid being expelled by evaporation and subsequent ignition, and weighed as sulphate of lime.

After the filtered liquid has been mixed with excess of ammonia, the magnesia is precipitated by phosphate of soda,

and the precipitate treated as in No. 6.

The quantity of carbonic acid contained in the mineral may be determined by loss. It may also be ascertained directly by means of the apparatus arranged for the quantitative determination of carbonic acid.

13. BONE-EARTH.

3 CaO, PO₅ with 3 MgO, PO₅ and CaO, CO₂.

A mass of white burnt bone is dissolved in dilute nitric acid, the solution digested for some time to expel all the carbonic acid, and the phosphates of lime and magnesia precipitated by ammonia. When the precipitate has separated, the solution, which contains the lime previously in combination with carbonic acid, is rapidly filtered, and the precipitate thoroughly washed with ammoniacal water.

From the filtrate, the lime is precipitated by oxalate of ammonia, and the precipitate treated as in No. 12.

The precipitate of phosphates of lime and magnesia is dissolved in the smallest possible quantity of hydrochloric acid, and the lime precipitated by neutral oxalate of potassa. The mixture is digested for some time at a gentle heat, to promote the separation of the precipitate, and the clear supernatant fluid is then cautiously neutralized with carbonate of potassa, in order to precipitate the oxalate of lime dissolved by the liberated oxalic acid; as soon as it has completely separated, the precipitate is filtered off. From the filtrate, which contains all the phosphoric acid and magnesia, the latter is precipitated by ammonia as phosphate of magnesia-ammonia, which is treated as in No. 6.

From the liquid filtered from this precipitate, which must contain free ammonia, the phosphoric acid is precipitated

by sulphate of magnesia.

Bone-earth may also be analyzed in the following manner. The finely-powdered substance is heated for a long time, nearly to boiling, with an excess of dilute sulphuric acid, the greater part of the water is then evaporated, and the mass mixed with twice its volume of absolute alcohol, which dissolves the phosphoric acid. The mixture is filtered, and the sulphates washed with alcohol. From these the sulphate of magnesia and a part of the sulphate of lime are extracted with water, and separated as in No. 12. The sulphate of lime remaining undissolved is ignited and weighed. The phosphoric acid solution is mixed with water, the alcohol evaporated, and the phosphoric acid then precipitated by sulphate of magnesia and ammonia as in No. 6.

A third method, based upon the insolubility of phosphate of binoxide of tin in nitric acid, is as follows: The weighed bone-ash is heated in a flask, with moderately strong nitric acid, and several times its weight of pure tin (tin-foil), the weight of which must be accurately known; the contents of the flask are heated to ebullition, diluted with water, and the binoxide of tin, which contains the

whole of the phosphoric acid, is filtered off, washed, dried, ignited and weighed. The difference between the weight of this precipitate and that of the binoxide of tin which should be furnished by the amount of metal employed, is due to phosphoric acid. The separation of the lime and magnesia contained in the solution is effected as in No. 12.

14. HEAVY-SPAR, CELESTINE, AND GYPSUM. BaO, SO₃.—SrO, SO₃.—CaO, SO₃ + 2 HO.

The water in gypsum is determined by ignition. Gypsum in fine powder is entirely converted into carbonate by heating with a solution of carbonate of soda; but the sulphates of baryta and strontia are only partly converted.

Hence these salts, in a state of fine powder, must be fused in a platinum crucible with three times their weight of carbonate of potassa and soda. The mass is then treated with boiling water, and the earthy carbonate filtered off at a boiling heat, and washed.

The filtered solution is carefully neutralized with hydrochloric acid, the sulphuric acid precipitated by chloride of barium, and the precipitate treated as in No. 3.

The earthy carbonates are dissolved in dilute nitric acid, taking care to obtain a nearly neutral solution, which is then evaporated to perfect dryness in a flask capable of being closed. The saline mass is treated with about twice its volume of absolute alcohol, with which it is allowed to digest, in the closed flask, for a long time, being constantly shaken, but not heated. The alcohol dissolves the nitrate of lime only. The mixture is filtered, and the two undissolved nitrates washed with absolute alcohol in a closely covered funnel.

The alcoholic solution is diluted with water, the greater part of the alcohol evaporated, and the lime precipitated, as in No. 12, by oxalate of ammonia.

The mixture of nitrates of baryta and strontia is dissolved in a little water, and the baryta precipitated by freshly-prepared hydrofluo-silicic acid, previously mixed with an equal volume of alcohol. The silico-fluoride of barium is collected on a weighed filter, washed with weak spirit, and dried.

The filtrate containing the strontia is mixed with sulphuric acid, evaporated to dryness, the sulphate of strontia ignited, and weighed.

If baryta and lime only are to be separated, the solution is largely diluted, the baryta precipitated by sulphuric acid, and the lime separated from the filtrate by oxalate of ammonia, after previously neutralizing with ammonia.

For the separation of baryta and strontia, neutral chromate of potassa may also be employed, which precipitates all the baryta as chromate; the latter is washed, dried, ignited and weighed. It is necessary, however, that the solution should be perfectly neutralized and largely diluted. The strontia may afterwards be precipitated by neutal carbonate of ammonia.

15. ALUMINA-ALUM.

KO, SO_3 ; Al_2O_3 , $3SO_3 + 24HO$.

A weighed quantity of the pure salt is dissolved in water, and the sulphuric acid precipitated by chloride of barium.

From the solution filtered from the sulphate of baryta, the alumina is precipitated, together with the excess of baryta which has been added, by a mixture of carbonate of ammonia and free ammonia. After gently heating for some time, the precipitate is filtered off, the solution evaporated, and the saline mass heated till all the chloride of ammonium is volatilized. The gently-ignited residue is chloride of potassium.

The precipitate containing alumina and baryta is dissolved in dilute hydrochloric acid, and the baryta precipitated by sulphuric acid.

From the solution filtered from the sulphate of baryta, the alumina is precipitated by carbonate of ammonia, or better, by sulphide of ammonium, either of which effects a more complete precipitation than caustic ammonia.

The precipitated hydrate of alumina is well washed, for which purpose hot water is to be preferred, and strongly ignited in order to expel the water.

The water contained in the alum is determined by loss. It may also be estimated directly by exposing the salt for a very long time to a gradually increasing heat, which must finally be raised to dull redness.

16. IRON-AMMONIA-ALUM.*

 NH_4O , SO_3 ; Fe_2O_3 , $3SO_3 + 24 HO$.

At a strong red heat, this salt is entirely decomposed, leaving pure sesquioxide of iron.

The determination of ammonia is effected as in No. 5; that of sulphuric acid according to No. 3.

* Powdered red or brown iron-stone is digested with concentrated sulphuric acid; the white sulphate thus produced is dissolved in water, the solution mixed with sulphate of ammonia, filtered and allowed to crystallize. In order to control the determination of the sesquioxide of iron, another portion of the salt is dissolved in water, and the sesquioxide precipitated by ammonia. The precipitated hydrate is washed, dried and ignited.

17. ALUMINA-CHROME-ALUM.*

$$\text{KO, SO}_3; \frac{\text{Cr}_2\text{O}_3}{\text{Al}_2\text{O}_3}$$
, $3 \text{ SO}_3 + 24 \text{ HO}$

The sulphuric acid is precipitated by chloride of barium as in No. 3.

The alumina, sesquioxide of chromium, and excess of baryta are precipitated from the filtrate by carbonate of ammonia mixed with caustic ammonia. After long standing, the precipitate is filtered off and thoroughly washed.

The filtrate is evaporated, the residue heated to expel chloride of ammonium, and the residual chloride of potassium gently ignited in a covered crucible.

The mixed precipitate is dried, ignited, and fused with about twice its weight of carbonate of soda and the same quantity of nitre, in a porcelain crucible, when all the chromium is converted into chromate of potassa; this is

* Three parts of finely-powdered bichromate of potassa are mixed with 15 parts of water, and 1 part of concentrated sulphuric acid is gradually added, so that no evolution of heat may ensue; sulphurous acid gas is then passed through the solution, which is kept cool, so that its temperature may not rise above 40°, until the odour of the gas begins to be perceptible. After some time, octohedra of pure chrome-alum are formed, which may be set aside. The mother-liquor is mixed with an equal volume of a solution of common alum, saturated at 40°, when the salt in question separates in yellowish octohedra.

extracted with water, and the residue of alumina and carbonate of baryta carefully washed.

The solution of alkaline chromate is carefully mixed with excess of hydrochloric acid and some alcohol, and heated until it has a pure emerald-green colour. The sesquioxide of chromium is precipitated from the hot solution by caustic ammonia, washed, dried, ignited and weighed.

The mixture of alumina and carbonate of baryta is dissolved in hydrochloric acid, the baryta precipitated by sulphuric acid, and afterwards the alumina by sulphide of ammonium (see No. 15).

18. PHOSPHORIC ACID AND ALUMINA.

I. The ignited and weighed alumina containing phosphoric acid is dissolved in concentrated hydrochloric acid, and tartaric acid added to the solution until it gives no precipitate with excess of ammonia. Chloride of ammonium and sulphate of magnesia are then added, the precipitated phosphate of magnesia-ammonia being treated as in No. 6. It generally contains a little alumina which may be separated by redissolving the precipitate, adding tartaric acid, and reprecipitating by ammonia.

II. The alumina containing phosphoric acid, after precipitation by ammonia, is dissolved in solution of caustic soda, the phosphoric acid precipitated from the diluted solution as phosphate of baryta, by chloride of barium, or baryta-water, caustic soda again added, the mixture heated nearly to the boiling-point, and filtered. The filtrate, containing alumina, is acidified, and the alumina precipitated, as directed in No. 15.

The baryta-precipitate is dissolved in hydrochloric acid,

the baryta precipitated by sulphuric acid, and afterwards the phosphoric acid by ammonia and sulphate of magnesia.

III. The freshly-precipitated alumina is dissolved in the smallest possible quantity of caustic soda, the solution diluted, heated to ebullition, and a solution of silicate of soda added as long as any precipitate of silicate of alumina is produced. Lastly, in order to precipitate the whole of the silicic acid, a concentrated solution of sal-ammoniac is added, the solution again boiled and filtered. From the filtrate, the phosphoric acid is precipitated by ammonia and sulphate of magnesia.

The silicate of alumina is decomposed by concentrated hydrochloric acid, the mass evaporated to dryness on the water-bath, the residue moistened with hydrochloric acid, the alumina-salt extracted with water, and the alumina

precipitated by carbonate of ammonia.

IV. The weighed alumina containing phosphoric acid is dissolved in concentrated nitric acid, and the solution heated with about the same quantity (accurately weighed) of pure tin (tin-foil). The mixture is diluted with water, heated until boiling, and the binoxide of tin which has combined with the whole of the phosphoric acid is filtered off, washed, and ignited. The difference between the weight of this precipitate and that of the binoxide of tin which should have been furnished by the metal employed, represents the phosphoric acid. The alumina is then precipitated from the solution by sulphide of ammonium.

19. ALUMINA AND SESQUIOXIDE OF IRON.

The mixture of the two is dissolved in hydrochloric acid, the greater part of the excess of acid evaporated, the solution mixed with an excess of pure solution of potassa and heated nearly to the boiling-point. The alumina is thus dissolved, the sesquioxide of iron being left behind of a dark brown colour. The solution is filtered off, acidulated with hydrochloric acid, and the alumina precipitated by sulphide of ammonium.

The sesquioxide of iron, which contains some potassa, is dissolved in hydrochloric acid, and re-precipitated by ammonia.

This method of separation is unsafe, and, unless repeated more than once, incomplete. It is better to heat the acid solution to ebullition, to add sulphite of soda, in order to reduce the sesquioxide of iron to the state of protoxide, to neutralize with carbonate of soda, and afterwards to boil with excess of caustic soda until the precipitate is black and pulverulent.

The solution is then filtered off, slightly acidulated with hydrochloric acid, and the alumina precipitated by sulphide of ammonium.

Another method of separation consists in heating the previously ignited precipitate to bright redness, in a little porcelain boat placed within a porcelain tube through which a stream of dry hydrogen is passed. The precipitate is allowed to cool in the stream of gas, and weighed. The amount of the sesquioxide of iron may be inferred from the loss of weight, and the result controlled by dissolving out the reduced iron with very dilute nitric acid, and weighing the residual alumina.

20. PHOSPHORIC ACID AND SESQUIOXIDE OF IRON.*

In order to separate phosphoric acid from sesquioxide of iron, the compound is ignited with at least an equal weight of carbonate of potassa and soda (No. 10), the resulting mass exhausted with water, the solution supersaturated with hydrochloric acid and then with ammonia, and the phosphoric acid precipitated by sulphate of magnesia.

The residual sesquioxide of iron retains some alkali.

Or the sesquioxide of iron containing phosphoric acid is dissolved in hydrochloric acid, precipitated by ammonia, and digested with excess of sulphide of ammonium (without previous filtration), until all the sesquioxide is converted into sulphide of iron. When the liquid is no longer green, but of a pure yellow colour, it is filtered off, and the phosphoric acid immediately precipitated by sulphate of magnesia.

For the accurate quantitative separation of a small quantity of phosphoric acid from a large quantity of sesquioxide of iron, the latter is dissolved in hydrochloric acid, and the solution heated to ebullition with sulphite of soda till its colour has changed to a bright green, when all the sesquioxide of iron is converted into protoxide. The solution is boiled till it no longer smells of sulphurous acid, neutralized with carbonate of soda, and, in order to produce a little sesquioxide of iron, mixed with a very little chlorinewater, the quantity of which must be regulated according to the amount of phosphoric acid which is present. The

^{*} For analyses for practice, the phosphate of sesquioxide of iron is prepared by precipitating sesquichloride of iron with phosphate of soda. Or a mixture of phosphates may be prepared by precipitating a solution containing sesquichloride of iron, chloride of calcium, chloride of magnesium, and chloride of manganese.

solution must now be mixed with an excess of acetate of soda, when phosphate of sesquioxide of iron separates as a white precipitate. Chlorine-water is then added, drop by drop, until the liquid has assumed a reddish colour, when it is boiled, so that the precipitate may collect, and be filtered. From this precipitate the phosphoric acid is separated by sulphide of ammonium, as directed above.

Or it may be dissolved in hydrochloric acid, boiled with sulphite of soda, and afterwards with excess of caustic soda, till the precipitate is converted into black proto-sesquioxide of iron, which is filtered off. The solution is acidified, and the phosphoric acid precipitated as above.

21. SPECULAR IRON, ${\rm Fe_2O_3}$, AND BROWN IRON-ORE, ${\rm Fe_2O_3}$, 3 HO.

For the determination of the water, weighed fragments of the iron-stone are heated to redness, for a long time, in a platinum crucible. If the mineral decrepitates, it must first be finely powdered.

In order to determine the oxygen, the fragments of ignited iron-stone or of specular iron are heated to redness in a weighed bulb-tube of very infusible glass (the bulb being as small as possible), through which a stream of dry hydrogen, free from arsenic, is transmitted as long as any water is formed. The reduction must be effected at the highest temperature of the spirit-lamp, for otherwise the reduced iron, even when cool, may reoxidize and sometimes inflame in the air. It is safer to reduce the oxide in a small porcelain boat, placed in a tube of porcelain, which is heated by a charcoal fire.

The reduced iron is dissolved in hydrochloric acid.

Silicic acid, which is often contained in brown iron-stone, is then left undissolved, and may be weighed.

22. MAGNETIC IRON-ORE.*

FeO, Fe₂O₃.

To determine the amount of oxygen which is combined with the iron, the proto-sesquioxide is reduced by hydrogen, as in No. 21.

If the substance contain only proto-sesquioxide of iron, the whole of the iron may be determined by dissolving in hydrochloric acid, heating with some chlorate of potassa, to convert all the protochloride into sesquichloride, and adding ammonia to precipitate the sesquioxide of iron, which is washed, dried, ignited and weighed.

If other constituents be present, the total amount of iron may be determined as follows: The substance is dissolved in an excess of hydrochloric acid, the protochloride converted into sesquichloride by addition of chlorate of potassa, and all free chlorine expelled by boiling. The solution is then diluted with water until the flask is more than half-full; a weighed strip of bright sheet-copper is placed in the solution, the flask closed by a cork furnished with a narrow glass tube, and the liquid heated to ebullition. It is retained at this temperature until the dark-brown colour originally observed has changed to a pale yellowish-green. The whole of the iron is now contained in the solution as protochloride, in consequence of the formation of subchloride of copper. The orifice of the little tube is closed air-tight, and the solution allowed

^{*} Smithy-scales have a similar composition.

to cool somewhat. The flask is then filled with hot water, the liquid poured off from the undissolved copper, which is to be washed, first with dilute hydrochloric acid, then repeatedly with water, dried, and weighed.—The atomic weight of copper is to that of iron as the quantity of copper dissolved is to that of the iron sought.

In order to determine directly the amount of protoxide and sesquioxide of iron present in a substance, it must be dissolved in hydrochloric acid. The following is the method adopted: The compound is dissolved in an excess of concentrated hydrochloric acid, in a flask filled with carbonic acid, and afterwards closed; the flask is then nearly filled up with water, previously boiled, and a weighed strip of copper introduced; the closed flask is placed in water, which must be gradually heated to boiling, the subsequent process being conducted and the result calculated as directed above.

Or the weighed substance is placed in a flask closed with a cork, and furnished with tubes for ingress and egress, and with a funnel-tube passing to the bottom of the flask, which is to be filled with carbonic acid. Hydrochloric acid is then added through the funnel-tube, and the solution assisted by heat, whilst carbonic acid is allowed to stream through the apparatus. The solution is afterwards diluted, through the funnel-tube, with boiled water, and a milky mixture of carbonate of baryta with water gradually added; this precipitates the whole of the sesquioxide of iron, while the protoxide remains in solution. When the supernatant liquid has become clear, it is decanted through the egresstube, the precipitate again mixed with water, and after the clear liquid has been again decanted, quickly thrown upon a filter, and rapidly washed, air being excluded, with water which has been previously boiled and allowed to cool.

The iron precipitate is dissolved in dilute hydrochloric acid, the baryta separated by sulphuric acid, and the sesquioxide of iron precipitated by ammonia.

The solution, which contains the protoxide of iron, is mixed with hydrochloric acid and chlorate of potassa, and concentrated by evaporation; the baryta is then precipitated by sulphuric acid, and afterwards the sesquioxide of iron by ammonia.

23. SPATHIC IRON-ORE.

FeO, CO₂, frequently containing MnO, CO₂,—CaO, CO₂, and MgO, CO₂.

I. The best method of analysis, which is especially applicable where but little manganese is present, is the following: A weighed portion of the powdered ore, previously dried, is dissolved in hydrochloric acid, with the aid of heat, nitrate or chlorate of potassa being added from time to time, so that the whole of the protoxide of iron is sure to be converted into sesquichloride. The solution, which must still be acid, so that chloride of ammonium may be formed, is diluted, and gradually neutralized with dilute ammonia, until it has acquired a dark brown-red colour, and a small quantity of hydrated sesquioxide of iron is precipitated. The whole of the sesquioxide of iron is then separated by neutral succinate of ammonia, while protoxide of manganese, lime and magnesia remain in solution. The precipitated succinate of sesquioxide of iron is rapidly filtered off, washed with cold water, dried, and gradually heated to redness in a porcelain crucible, with free access of air, till it is converted into pure sesquioxide of iron.

The filtrate is feebly acidulated with hydrochloric acid, evaporated to dryness, and heated till all ammoniacal salts are expelled.

The residue is then dissolved in a small quantity of water, with addition of hydrochloric acid, the solution saturated with chlorine, and the manganese precipitated as hydrated sesquioxide by addition of ammonia. The liquid is rapidly filtered off, so that no carbonate of lime may be precipitated, and the manganese-precipitate washed, dried, and ignited, when it is converted into proto-sesquioxide.

The lime and magnesia in the filtrate are separated as in No. 12.

Or the manganese may be precipitated by sulphide of ammonium, the sulphide of manganese rapidly filtered off, and dissolved in hydrochloric acid. When all the sulphuretted hydrogen has been expelled by evaporation, the solution is heated with carbonate of soda, when the manganese is precipitated as carbonate, which, after ignition, leaves the proto-sesquioxide.

From the solution filtered from the sulphide of manganese, the lime and magnesia are precipitated as in No. 12.

II. The acid solution is largely diluted with water, and carbonate of soda gradually added (drop by drop, when the solution is neutral), with constant stirring, until all the sesquioxide of iron is precipitated. The other bases remain dissolved in the free carbonic acid. The manganese is then best precipitated by hypochlorite of soda, in the cold.

III. When a larger quantity of manganese is present, the solution, which must contain the iron entirely in the form of sesquichloride, and must not be too acid, is gradually mixed with carbonate of baryta, which precipitates the sesquioxide of iron only. When a slight excess of carbonate of

baryta has been added, and the solution well stirred, it is filtered. The washed precipitate is dissolved in dilute hydrochloric acid, the baryta precipitated by sulphuric acid, and the sesquioxide of iron by ammonia.

From the solution which contains the other three bases, the dissolved baryta is first precipitated by sulphuric acid, and the solution treated as in No. 12.

IV. The diluted solution, obtained as in I, is neutralized with carbonate of soda till it has a dark brown-red colour, mixed with a saturated solution of acetate of soda, and heated to ebullition, when the whole of the sesquioxide of iron is precipitated.

The filtrate is neutralized with carbonate of soda, mixed with hypochlorite of soda (containing bicarbonate of soda), and allowed to stand, in a closed vessel, for twenty-four hours, when the manganese is precipitated as hydrated sesquioxide, which is ignited and weighed as proto-sesquioxide.

From the filtered liquid the lime and magnesia are separated as above.

24. BOG-IRON-ORE.

 $\mathrm{Fe_2O_3}$ with MnO, $\mathrm{Al_2O_3},~\mathrm{CaO},~\mathrm{MgO},~\mathrm{SiO_3},~\mathrm{PO_5},~\mathrm{AsO_5}.$

If the amount of iron only is to be determined, the process with copper may be employed, as in the case of magnetic iron; or the ore may be subjected to the dry assay. The complete analysis is effected in the following manner:

I. The mineral, dried at 100°, is ignited, and the water determined.

II. Another portion, which has not been ignited, is

coarsely powdered, and dissolved in hydrochloric acid; the solution is evaporated to perfect dryness on the waterbath, the mass dissolved in warm dilute hydrochloric acid, and the sand and silicic acid removed by filtration. The latter may, after ignition and weighing, be separated from the sand by boiling with carbonate of soda.

III. The hydrochloric solution is boiled with an alkaline sulphite, until it no longer smells of sulphurous acid, to reduce the sesquichloride of iron to protochloride, and the arsenic acid to arsenious acid, which is then precipitated by sulphuretted hydrogen, as tersulphide of arsenic; sometimes mixed with a little sulphide of copper.

IV. The solution is boiled till the sulphuretted hydrogen is completely expelled, precipitated by carbonate of soda, mixed with an excess of caustic soda, and boiled until the precipitate becomes pulverulent.

V. The solution is filtered off. It contains all the alumina and part of the phosphoric acid, which are separated as in No. 18.

VI. The precipitate, consisting of proto-sesquioxide of iron, carbonate of protoxide of manganese, carbonate and phosphate of lime and magnesia, is dissolved in hot nitric acid; the solution is neutralized, as far as possible, with carbonate of soda, mixed with acetate of soda, and boiled, when all the phosphoric acid and sesquioxide of iron are precipitated. In order to separate these, the precipitate is treated as in No. 20.

VII. The filtrate contains the protoxide of manganese, lime, and magnesia, which are separated as in No. 23.

25. SULPHATE OF COPPER. CuO, $SO_3 + 5$ HO.

For analysis, the salt is purified by recrystallization.

To determine the water, a weighed quantity of the dry salt, in the state of fine powder, is heated to about 200°, until it has become perfectly white, and has ceased to lose weight.

It is then dissolved in water, and the sulphuric acid precipitated by chloride of barium, as directed in No. 3.

For the determination of copper, another weighed portion of the salt is dissolved in from 50 to 100 times its weight of water, in a dish or a wide-mouthed flask; the solution is heated until boiling, and the oxide of copper precipitated by caustic potassa, which should not be added in too large excess. The brownish-black precipitate is filtered off, washed with hot water, dried and weighed.

To determine the amount of oxygen in the oxide of copper, a freshly-ignited portion is introduced into a weighed bulb-tube, and its weight carefully ascertained; a stream of dry hydrogen, free from arsenic, is then passed through the tube, the bulb of which is heated to redness with a large spirit-lamp flame. When no more aqueous vapour is perceptible, and the oxide is completely reduced to the metallic state, it is allowed to cool in the stream of gas, and weighed as soon as the hydrogen in the tube has been replaced by atmospheric air.

26. COPPER-PYRITES.

Cu₂S, Fe₂S₃.

The powdered mineral is introduced into a flask, placed obliquely, and gradually mixed with concentrated nitric

acid, added in small portions at a time; the contents of the flask are then heated until either the whole is dissolved, or the metals have passed into solution together with a portion of the sulphur, and the unoxidized sulphur has separated in the form of a yellow powder, or in fused drops of a clear yellow colour. The solution is diluted with water, and decanted from any undissolved sulphur, which is well washed, dried in a porcelain crucible, at a gentle heat, and weighed. It is then burnt in order to ascertain whether it contains any metal or quartz, &c. Should the sulphur be separated in a pulverulent state, it must be collected on a weighed filter, washed, and dried at a very gentle heat.

From the filtered solution, that portion of the sulphur which has been converted into sulphuric acid is precipitated by chloride of barium, and the sulphate of baryta treated as in No. 3. Protracted washing with hot water is necessary, since the precipitate has carried down some nitrate of baryta.

In order to avoid this, the mineral may be dissolved in concentrated hydrochloric acid, with gradual addition of nitric acid, or of chlorate of potassa.

The excess of baryta having been removed from the liquid filtered from the sulphate of baryta by means of sulphuric acid, a slow stream of sulphuretted hydrogen is passed through the filtrate, until the odour of the gas is distinctly perceptible. The precipitated sulphide of copper is thrown, as rapidly as possible, upon a dried and weighed filter, and well washed with water containing sulphuretted hydrogen.

It is then dried in the funnel at 200°, weighed, a portion of it introduced into a weighed bulb-tube, which is afterwards again weighed, and heated in a stream of hydrogen until it no longer loses any sulphur. It is thus

converted into Cu₂S, which contains the same amount of copper as the protoxide. The weight obtained is calculated upon the whole quantity of sulphide of copper.

Or the filter with its contents may be allowed to dry in the funnel, the precipitate detached, and thrown into a beaker; the filter is then completely incinerated, the ash added to the sulphide of copper, and the latter oxidized with aqua-regia till the sulphur separates of a pure yellow colour. From the filtered solution, the protoxide of copper is precipitated at a boiling heat by caustic potassa, ignited and weighed.

The solution filtered from the sulphide of copper, containing the iron in the form of protoxide, is heated nearly to boiling, in a flask, concentrated if necessary by evaporation, and treated at the same time with chlorate of potassa in small portions, until all the protoxide of iron is converted into sesquioxide, which is then precipitated by ammonia, washed, dried and ignited.

Notwithstanding the solubility of oxide of copper in caustic ammonia, this reagent will not effect its complete separation from sesquioxide of iron, since the latter carries down with it a considerable quantity of oxide of copper which cannot be extracted by ammonia.

27. ZINC-BLENDE.

ZnS.

The solution is effected just as in the case of copperpyrites. The mineral must be very finely powdered, and very concentrated acid must be employed.

After the sulphuric acid which is produced has been precipitated by chloride of barium, and the excess of

baryta has been removed, the solution is saturated with sulphuretted hydrogen, in order to precipitate any copper and cadmium which often occur in small quantities in this mineral. The precipitate, after being filtered off and washed, is dissolved, together with the filter, in nitric acid, the solution mixed with excess of potassa, and afterwards with as much hydrocyanic acid as is required to dissolve the precipitate. From this solution, containing the cadmium and copper in the form of double cyanides, the cadmium is precipitated by sulphuretted hydrogen, while the copper is left in solution. This solution is then boiled with aqua-regia, and the oxide of copper precipitated from the hot solution by potassa. For the method of treating the sulphide of cadmium, see Zinc and Cadmium.

The first filtrate, which contains the zinc and generally a little iron, is heated to ebullition, and mixed, first with some hypochlorite of soda to peroxidize the iron, then with excess of ammonia, until all the oxide of zinc is redissolved, and the sesquioxide of iron precipitated; the latter is then washed and ignited. It cannot be obtained by this method perfectly free from oxide of zinc.

From the filtrate, the zinc is precipitated by sulphide of ammonium. The precipitate should not be filtered off until it has separated from the liquid; it is washed with water containing a little sulphide of ammonium, and digested (together with the filter), while yet moist, with concentrated hydrochloric acid, the solution filtered off, and the oxide of zinc precipitated, at the boiling-point, by carbonate of soda. The precipitate is washed, dried, ignited, and weighed as pure oxide of zinc.

Sesquioxide of iron may be more completely separated from oxide of zinc by means of succinate of ammonia, as described in No. 23, or by carbonate of baryta (No. 23, III.) If, as has been proposed, the solution were mixed with acetate of soda, so as to convert the iron and zinc into acetates, and treated with sulphuretted hydrogen, not only zinc, but iron also would be precipitated.

28. CALAMINE.

ZnO, CO2.

Common calamine generally contains small quantities of protoxides of iron, manganese, lead and cadmium, together with lime, magnesia and silicic acid.

It is dissolved in hydrochloric acid, the solution evaporated to dryness, the mass digested with concentrated hydrochloric acid, diluted, heated, and the silicic acid filtered off.

The solution, which must be acid, is saturated with sulphuretted hydrogen, which precipitates the lead and cadmium.

This precipitate is oxidized with concentrated nitric acid, a little sulphuric acid being also added, evaporated to dryness, and the sulphate of cadmium separated from the sulphate of lead by water. (See Lead and Bismuth.)

The filtrate is boiled, to expel the sulphuretted hydrogen, and treated with chlorate of potassa to peroxidize the iron. From the solution, which must still contain free chlorine, the sesquioxides of iron and manganese are precipitated by excess of caustic ammonia, and separated as in No. 23.

The zinc is precipitated from the filtered solution, as sulphide, by addition of sulphide of ammonium, and the precipitate treated as in No. 27. The solution is rapidly filtered off, with as little exposure to air as possible, and

the lime precipitated by oxalate of ammonia; the magnesia is afterwards separated by phosphate of soda.

If a specimen of calamine consist of carbonate and silicate of zinc, their relative quantities may be approximately determined by igniting the finely-powdered mineral, and digesting it with a mixture of carbonate of ammonia and free ammonia, which dissolves the oxide of zinc previously in combination with carbonic acid, leaving the silicate untouched.

29. SULPHATE OF IRON WITH THE SULPHATES OF COPPER AND ZINC.

FeO, SO₃ with CuO, SO₃,—ZnO, SO₃ and HO.

The aqueous solution is strongly acidified with hydrochloric acid, and the copper precipitated by sulphuretted hydrogen. (See No. 25.)

The iron and zinc are then separated and determined as in No. 27.

Or the solution may be treated with hypochlorite of soda to peroxidize the iron, afterwards neutralized with carbonate of soda till it has become of a dark red colour, mixed with acetate of soda, and boiled until all the sesquioxide of iron is precipitated. With the latter, however, a small quantity of zinc is usually precipitated by this method.

30. BRASS.

The alloy is dissolved in hydrochloric acid with gradual addition of nitric acid, the solution diluted, and the copper precipitated by sulphuretted hydrogen. (See No. 25.)

38 BRASS.

The excess of sulphuretted hydrogen is expelled from the filtrate by boiling, and the oxide of zinc precipitated from the hot solution by carbonate of soda. (See No. 27.)

Oxide of zinc cannot be entirely separated from oxide of copper by even a very large excess of caustic potassa.

Too little zinc is usually obtained by the above process, because a portion is carried down with the sulphide of copper. The separation is more completely effected by neutralizing the diluted solution of the alloy with ammonia, and digesting with a slight excess of solid hydrate of potassa until it has lost its colour and ammoniacal odour. The oxide of copper is then filtered off, and washed with hot water. From the alkaline solution, the zinc is precipitated by sulphide of ammonium.

The brass sometimes contains traces of tin, It is then dissolved in hot nitric acid, which leaves the binoxide of

tin (containing a little copper) untouched.

In order to detect a small quantity of lead which frequently occurs in brass, the sulphide of copper precipitated by sulphuretted hydrogen is oxidized with fuming nitric acid, the mass dried, and treated with water, which leaves the sulphate of lead undissolved. Should this contain sulphur, it must be burnt off.

Or the brass may be dissolved in nitric acid, a little sulphuric acid added, the solution evaporated to dryness, and the mass treated with water.

If the brass be placed in a little porcelain boat, and heated to redness in a porcelain tube through which a rapid stream of hydrogen is passed, all the zinc may be volatilized.

31. OXIDES OF MANGANESE, IRON, AND ZINC.

The solution, which must contain the iron in the form of sesquioxide, is mixed with carbonate of soda until a permanent precipitate begins to appear; it is then boiled with acetate of soda, when all the sesquioxide of iron is precipitated.

The filtrate is mixed with acetic acid, and the zinc preci-

pitated by sulphuretted hydrogen.

The manganese may be precipitated, after neutralization, with an alkaline hypochlorite, or by boiling with an alkaline carbonate.

32. CADMIUM AND ZINC.

The alloy of the two metals is dissolved in hydrochloric acid, the solution, which must be decidedly acid, is largely diluted, and saturated with a slow stream of sulphuretted hydrogen, which precipitates all the cadmium in the form of a yellow sulphide. The latter is thrown upon a weighed filter, and dried at 100° till of constant weight.

It is more accurate to dissolve the sulphide of cadmium in hydrochloric or nitric acid, and to precipitate the oxide of cadmium from the solution, as white carbonate, by means of carbonate of soda. The precipitate is washed, dried and ignited, when it is converted into the brown oxide. Previously to the incineration of the filter, the precipitate should be detached, as far as possible.

The filtrate is boiled to expel the sulphuretted hydrogen, and the zinc precipitated from the hot liquid by carbonate

of soda.

Another method consists in precipitating the cadmium from the solution containing the two metals, by carbonate of baryta.

An approximative separation of the two metals may be also effected by mixing the solution with an excess of ammonia till the precipitate is completely redissolved, adding a saturated solution of sulphurous acid, and boiling till the excess of the latter is expelled. The cadmium is then precipitated as a white, crystalline, double sulphite of ammonia and oxide of cadmium, while the zinc remains in solution.

33. GALENA.

PbS.

The finely-powdered mineral, placed in a capacious dish, is gradually moistened with fuming nitric acid until it is entirely converted into white sulphate of lead; a few drops of sulphuric acid are added, to ensure complete conversion, the mass ignited and weighed.

If the residue, previously to ignition, be treated with water, and filtered, only traces of lead are found in the solution. If the galena contain copper, iron or silver, they will be detected in the solution, the two first by ammonia and the silver by hydrochloric acid.

If the galena be oxidized with more diluted nitric acid, the residue consists of a mixture of sulphate of lead and sulphur, while the solution contains nitrate of lead, from which the lead may be precipitated by sulphuric acid, or, more completely, by oxalate of ammonia, after neutralization. By igniting the dried residue, the sulphur is volatilized, and sulphate of lead remains.

When boiled with a solution of carbonate of soda, the sulphate of lead is converted into carbonate, which, after washing, is completely dissolved by nitric acid.

Sulphate of lead is dissolved to a great extent by a mixture of tartrate of ammonia and free ammonia. From this solution it may be completely precipitated by sulphide of ammonium as black sulphide of lead, or by chromate of potassa, in the form of yellow chromate of lead.

34. WHITE LEAD.

2 (PbO, CO_2) + PbO, HO frequently mixed with BaO, SO_3 ,—CaO, SO_3 ,—CaO, CO_2 , or PbO, SO_3 .

Pure white lead is perfectly soluble in dilute nitric acid. The oxide of lead may be determined by ignition, after drying at 100°. In order to estimate the water, a specimen, which has been dried at 100°, is ignited in a tube to which a weighed chloride-of-calcium-tube is attached. The carbonic acid, which is expelled at the same time, is determined by loss. White lead sometimes contains a small quantity of basic acetate of lead, indicated by the odour of acetone which is perceived when the specimen is ignited.

White lead adulterated with chalk is likewise dissolved, with exception of traces of impurities, by nitric acid. From the diluted solution, the lead is precipitated by sulphuretted hydrogen, the sulphide of lead collected upon a weighed filter, washed, dried at 100°, and weighed.—From the solution, after neutralizing with ammonia, the lime is precipitated by oxalate of ammonia.

If heavy-spar be present in the specimen, it is left behind

on treatment with nitric acid. After washing and igniting, it is weighed and analyzed as in No. 14.

Gypsum would also be in great measure left behind on dissolving in nitric acid. It may, however, be entirely dissolved and separated from any heavy-spar present at the same time, by boiling with a large quantity of dilute nitric acid. The amount of gypsum present may be inferred from that of the sulphate of baryta obtained by precipitating the solution with chloride of barium.

Sulphate of lead would also be left undissolved by dilute nitric acid. After washing, it becomes black when treated with sulphide of ammonium; it is soluble in tartrate of ammonia mixed with free ammonia. In a mixture of sulphate of lead and sulphate of baryta, the former may be converted, by digestion with sulphide of ammonium, into sulphide of lead, which can be transformed into chloride by treatment with concentrated hydrochloric acid, and may then be dissolved out by water.

35. PYROMORPHITE. 3 (3 PbO, PO₅) + PbCl.*

In many varieties, the chloride of lead is replaced by chloride of calcium, in others, a part of the phosphoric acid is replaced by arsenic acid. The green varieties contain traces of sesquioxide of iron and sesquioxide of chromium or chromic acid.

* May be artificially obtained in crystals, by fusing in a porcelain crucible an intimate mixture of 1 part of fused phosphate of soda, and 7 parts of chloride of lead; the mass is very gradually heated to about the fusing-point of the latter; it is then allowed to cool, and the liquid portion decanted from the crystals.

Those specimens which are free from lime are finely powdered, and dissolved in caustic potassa. The lead is precipitated from the solution by sulphide of ammonium, the precipitate collected upon a weighed filter, dried at 100°, and weighed.

The filtered solution is acidified with hydrochloric acid, which precipitates any sulphide of arsenic, to be treated as directed in the article upon copper-nickel (No. 59).

The liquid filtered from the sulphide of arsenic is con-

The liquid filtered from the sulphide of arsenic is concentrated by evaporation, supersaturated with ammonia, and the phosphoric acid precipitated by sulphate of magnesia.

The chlorine is determined in another portion, by dissolving in nitric acid, and precipitating by nitrate of silver.

For the determination of lime, the mineral is dissolved in nitric acid, and the lead precipitated from the diluted solution by sulphuretted hydrogen. The solution filtered from the sulphide of lead is neutralized with ammonia, and the lime precipitated by oxalate of ammonia. The filtrate is concentrated by evaporation, mixed with ammonia, and the phosphoric acid precipitated by sulphate of magnesia.

Those specimens which are free from lime, but which contain arsenic acid, may be analyzed in the following manner. The mineral, in a state of very fine powder, is digested with moderately dilute sulphuric acid, the greater part of the water evaporated, the mass mixed with alcohol, and the sulphate of lead thrown upon a filter and washed with spirit of wine. The filtrate is evaporated to expel the alcohol, and a stream of sulphuretted hydrogen passed through it, while it is heated to about 50°. It is afterwards allowed to cool while the gas is still passing, and,

when saturated with sulphuretted hydrogen, set aside in a closed vessel for twenty-four hours, after which the precipitated pentasulphide of arsenic is filtered off.

The filtered solution is treated with ammonia which precipitates the iron as sulphide, occasionally mixed with a small quantity of sesquioxide of chromium.

The phosphoric acid is precipitated from the filtrate, after concentration, by sulphate of magnesia and ammonia.

In order to separate the sesquioxide of chromium, the mineral is digested with a mixture of concentrated hydrochloric acid and alcohol, the solution filtered, evaporated to expel the alcohol, and the sesquioxide of chromium precipitated from the hot solution by ammonia. It still contains a little phosphoric acid.

36. SILVER AND LEAD.

I. By cupellation.

II. The solution of the two metals in nitric acid is diluted with much water, heated nearly to the boiling-point, and the silver precipitated as chloride of silver by hydrochloric acid. (See No. 1.)

The filtered solution is allowed to cool, the greater part of the acid neutralized with ammonia, and the lead precipitated by sulphuretted hydrogen.

III. The diluted nitric solution of the two metals is mixed with dilute hydrocyanic acid which precipitates the silver as cyanide. When this has accumulated, leaving the solution clear, it is collected upon a filter which has been dried at 120°, washed, dried at that temperature, and weighed.

From the filtrate, after neutralizing the larger excess of

acid, the lead may be precipitated by sulphuretted hydrogen, or if the solution be concentrated by evaporation, by

sulphuric acid in the presence of alcohol.

IV. Another method consists in precipitating the solution of the two metals by a slight excess of carbonate of soda, and digesting the precipitate with cyanide of potassium, which dissolves the silver in the form of a double cyanide, leaving the carbonate of lead untouched. Since, however, it contains some alkali, it must be dissolved in nitric acid, and precipitated by sulphuretted hydrogen or sulphuric acid. From the solution containing the silver, the latter may be precipitated as cyanide by nitric acid.

V. The solution of the lead and silver in nitric acid is neutralized with an alkali, mixed with an alkaline formate, and heated to boiling, when all the silver is preci-

pitated in the metallic state.

37. SILVER AND COPPER.

(Silver-coin.)

The alloy is dissolved in moderately strong nitric acid, the silver precipitated from the hot solution by dilute hydrochloric acid with violent agitation, and the chloride of silver treated as in No. 1.

The oxide of copper is precipitated from the filtrate by caustic potassa at a boiling-heat, washed, dried, ignited and weighed, the filter being completely incinerated apart from the precipitate.

If the alloy contain gold also, it is left behind by the nitric acid as a brown powder. If it be present in very small quantities—as, for example, in all old silver coins—

the small insoluble residue is filtered off, thoroughly washed, the filter incinerated, and the ash fused before the blowpipe with carbonate of soda, when the gold appears in small globules.

In order to prepare pure silver, it is precipitated from the solution by hydrochloric acid or chloride of sodium, in the form of chloride which is well washed and fused in a porcelain capsule. A fragment of zinc is placed upon the fused mass, and some dilute hydrochloric acid poured over it. After twenty-four hours, the chloride of silver is completely reduced; the spongy masses of silver are rinsed out, rubbed to a fine powder under water, and digested with dilute hydrochloric acid, to remove any zinc. It is then thoroughly washed and fused with borax to a reguline mass.

Or the dry chloride of silver may be mixed with an equal quantity of anhydrous carbonate of soda, and the mixture introduced into a crucible, the bottom and sides of which are coated with as thick a layer as possible of carbonate of soda. The crucible is then heated for a length of time to low redness, and afterwards to the fusing-point of silver.

Another plan is to mix the chloride of silver with \(\frac{1}{3} \) its weight colophony, to heat gently until the resin is perfectly carbonized, and, after adding some borax, to raise the heat until the silver fuses.

It is less effective to boil the chloride of silver, which must be freshly precipitated, with strong solution of potassa, which converts it into black oxide; or with potassa and solution of sugar, which reduces it to the metallic state.

The original solution containing copper may also be mixed with ammonia in excess, and the silver precipitated by a plate of copper; or sulphurous acid gas may be passed into the ammoniacal solution, and the silver thus precipitated in the metallic state.

38. GOLD AND COPPER.

(Coins.)

I. The alloy is dissolved in a mixture of hydrochloric and nitric acids, care being taken that none of the latter shall remain undecomposed after the solution is effected; the liquid is heated with oxalic acid, which precipitates all the gold in the metallic state. It is washed, dried, transferred to a porcelain crucible, the filter completely incinerated, and the gold, together with the ashes, ignited and weighed. From the filtrate the copper may be precipitated by sulphuretted hydrogen, or by potassa at a boiling-heat.

II. The gold is first precipitated by a solution of pure protosulphate of iron, and the copper is afterwards separated from the solution, either by sulphuretted hydrogen, or by a piece of bright iron placed in the liquid, which must not be too acid, and should be heated nearly to boiling. The precipitated copper is washed, dried, and ignited in air, when it is converted into oxide.

39. GOLD AND SILVER.

I. From an alloy containing less than about 15 per cent of silver, aqua-regia dissolves all the gold, while the whole of the silver is left as chloride; for this purpose, however, the metal must be employed in a very thinly laminated state. The solution is evaporated, to expel as much of the nitric acid as possible; and diluted with water, to effect

the complete separation of the chloride of silver. From the solution the gold is precipitated by oxalic acid, or by protosulphate of iron.

II. If the alloy contain more than 80 per cent of silver, pure nitric acid dissolves the whole of the silver, and leaves the gold. Here also the alloy must be thinly laminated. The silver is precipitated by hydrochloric acid. The gold is well washed, and dissolved in aqua-regia, to ascertain if any trace of silver be left in it.

III. When the quantity of silver present in the alloy is between 15 and 80 per cent, it cannot be entirely extracted by nitric acid, neither can all the gold by dissolved out by aqua-regia, since the metal becomes covered with a thick layer of chloride of silver. Such an alloy should be fused in a porcelain crucible with 3 times its weight of pure lead. From this alloy, nitric acid then dissolves all the lead and silver, leaving pure gold.

From the solution filtered from the gold, the silver is precipitated by hydrocyanic acid; or, after diluting largely, and heating nearly to boiling, by hydrochloric acid.

IV. Silver and gold in alloys of these metals may also be separated (parted) by concentrated sulphuric acid, whatever may be the relative proportion of the two metals. The thinly laminated alloy is heated with the acid in a capacious dish, until all evolution of gas ceases, and the acid begins to evaporate. The sulphate of silver which is produced is then dissolved in the requisite quantity of hot water, and the solution decanted from the gold, which, for greater certainty, is once more heated with a small quantity of sulphuric acid; afterwards thoroughly washed, ignited and weighed.

V. All such alloys may be also conveniently analyzed by fusion with bisulphate of potassa.

40. AMALGAMS.

The following amalgams may be analyzed by heating very gradually in a porcelain crucible, finally raising the heat to redness, till the mercury is entirely volatilized, and the tin or copper oxidized. To ensure complete oxidation, the mass is ultimately moistened with concentrated nitric acid, and again ignited. The amalgam of silver leaves the latter in the metallic state. In order to estimate the mercury also directly, the following method is adopted:

I. AMALGAM OF COPPER.*—The amalgam is dissolved in aqua-regia, the solution neutralized, though not completely, with potassa, mixed with formiate or sulphite of potassa or soda, and allowed to stand for some time at a temperature between 50° and 60°. All the mercury is thus precipitated as subchloride. Above 60°, metallic mercury would also be separated. The subchloride of mercury is collected upon a filter, which has been dried at 100° and weighed, and its weight determined after drying at 100°.

From the filtered solution the oxide of copper is precipitated, at a boiling heat, by caustic potassa.

II. AMALGAM OF TIN (amalgam for mirrors).—This is dissolved in aqua-regia, the solution mixed with ammonia in slight excess, afterwards with an excess of sulphide of ammonium, and digested for a long time in a closed vessel. The bisulphide of tin which is formed dissolves in the sul-

^{*} This amalgam, which is semi-fluid at 100°, but solid and crystalline at the ordinary temperature, is obtained when copper, which has been precipitated by iron, is moistened with nitrate of suboxide of mercury, and triturated in a warm mortar with mercury, added by degrees, until the amalgam has the consistence of butter.

phide of ammonium, and the black sulphide of mercury separates; it is collected upon a weighed filter, washed with weak sulphide of ammonium, and dried at 100°.

From the solution in sulphide of ammonium the bisulphide of tin is precipitated by dilute hydrochloric acid, filtered off, washed, dried, and roasted, together with the filter, in a porcelain crucible, with free access of air. A gentle heat is at first applied, which is gradually increased, till the whole of the precipitate is converted into white binoxide of tin; a fragment of carbonate of ammonia is held in the ignited crucible at the end of the operation.

If it be desired to determine the mercury alone, it may be precipitated from the solution of the amalgam in aquaregia by means of protochloride of tin, as in the case of the amalgam of silver.

III. AMALGAM OF SILVER.*—The amalgam is dissolved, by the aid of heat, in nitric acid, so that the solution may contain the whole of the mercury in the state of protoxide; the acid solution is diluted with water, and the silver precipitated by an excess of hydrochloric acid.

The solution filtered from the chloride of silver is concentrated by evaporation, with addition of some strong hydrochloric acid, to decompose all the nitric acid. The mercury is then precipitated by sulphuretted hydrogen, and the precipitate dried at 100°.

Or the solution containing the mercury may be mixed with an acid solution of protochloride of tin, and heated nearly to boiling, when all the mercury is precipitated in the metallic state, either as a greyish-black powder, or

^{*} May be obtained in crystals by allowing a small quantity of mercury to remain in a moderately diluted solution of nitrate of silver, or by placing a thick bright copper-wire in the mixed solutions of nitrate of silver and of suboxide of mercury.

in minute globules. The clear liquid is decanted from the metal, and concentrated hydrochloric acid poured over it, when it unites, especially on heating, into larger globules, which may be washed, and dried in a weighed vessel over sulphuric acid.

Another method consists in neutralizing the solution of the amalgam with potassa, and adding excess of cyanide of potassium, or hydrocyanic acid and potassa; from the solution of the double cyanides thus formed, the cyanide of silver is precipitated by nitric acid, dried at 100° upon a weighed filter, and the mercury then precipitated by sulphuretted hydrogen.

41. MIXTURES OF PROTOXIDE OF MERCURY, MINIUM, AND CINNABAR.

By digesting with dilute nitric acid, the protoxide of mercury is extracted, together with a portion of the protoxide of lead, the remainder of the lead being left behind in the form of brown binoxide, mixed with the cinnabar. This residue is well washed upon a weighed filter.

From the solution, which must contain an excess of nitric acid, the lead is precipitated by an excess of sulphuric acid, and the mercury then separated by sulphuretted hydrogen or protochloride of tin, the solution having been previously freed from nitric acid by evaporation with concentrated hydrochloric acid. (See Amalgams.)

The mixture of cinnabar and binoxide of lead is treated, upon the filter, with a warm mixture of dilute nitric acid and a little oxalic acid, which dissolves the binoxide of lead, with evolution of carbonic acid. The cinnabar is then washed, dried at 100°, and weighed.

The lead is precipitated from the solution by sulphuric acid, with addition of some alcohol.

In order to analyze the cinnabar, it is dissolved (in this case, together with the filter) in concentrated hydrochloric acid, with careful addition of chlorate of potassa; the sulphuric acid is then precipitated from the diluted solution by chloride of barium, the filtrate concentrated, and the mercury precipitated by protochloride of tin.

42. TIN AND COPPER.

(Bronze, Gun-metal, Bell-metal.)

I. The alloy, as finely divided as possible, is oxidized with concentrated nitric acid, the greater excess of the latter evaporated, the solution diluted with hot water, and the undissolved binoxide of tin filtered off. The copper is precipitated from the filtrate by caustic potassa, at a boiling-heat.

If the bronze contain also zinc, lead and iron, the lead is precipitated by sulphuric acid, and the copper by sulphuretted hydrogen. The solution filtered from the sulphide of copper is heated with some chlorate of potassa in order to peroxidize the iron, and the sesquioxide of the latter metal precipitated by an excess of ammonia. The oxide of zinc remains dissolved in the alkali, and is precipitated by sulphide of ammonium. Or the method described in No. 27 may be followed.

II. A surer method of obtaining the binoxide of tin free from other metals consists in dissolving the alloy in weak aqua-regia, precipitating with carbonate of soda, heating to ebullition, and subsequently acidifying the liquid with nitric acid, and allowing it to digest for some time. The binoxide

of tin is thus separated, while copper and other metals remain dissolved.

III. A very accurate analysis may also be effected by heating the alloy in a current of dry chlorine, when the tin and a part of the iron are volatilized as chlorides, which are conducted into water, and chloride of copper, chloride of zinc, and chloride of lead are left. (See Fahl-ore.)

43. TIN AND LEAD.

(Pewter, Soft Solder.)

The alloy is oxidized with moderately strong nitric acid, which leaves the tin undissolved in the form of binoxide; after heating and diluting with water, the binoxide of tin is filtered off, washed, dried and ignited.

From the filtrate the lead is precipitated by dilute sulphuric acid. The whole solution, containing the suspended precipitate, is evaporated to expel the nitric acid, until the sulphuric acid begins to volatilize; it is then diluted with water, and the sulphate of lead collected upon a weighed filter, which has been dried at 120°, and washed with spirit of wine. A filter which has not been weighed may be employed, if care be taken to remove as much as possible of the precipitate from the filter, and to incinerate the latter carefully apart, so that no reduction of lead may take place. (Moreover, see No. 44.)

44. BISMUTH, LEAD, AND TIN.

The alloy is oxidized with moderately strong nitric acid, the mass mixed with an excess of ammonia and sulphide of ammonium, and digested for some time in a closed flask. In this way the tin is entirely dissolved as a sulphur-salt. The solution is filtered off from the other sulphides, which are then washed with very weak sulphide of ammonium, and dried.

From the solution the bisulphide of tin is precipitated by dilute hydrochloric acid, filtered off, washed and dried. It is then gradually heated, together with the filter, in a porcelain crucible, with free access of air; at first gently, and ultimately to redness, so that it may be entirely converted into binoxide of tin. A fragment of carbonate of ammonia is held in the crucible at the end of the operation, to remove any sulphuric acid which may have been formed.

The mixture of sulphide of bismuth and sulphide of lead is detached, as far as possible, from the filter, the latter incinerated, and the ash added to the precipitate which is then oxidized in a capacious capsule, with concentrated nitric acid, a little sulphuric acid added lest there should not be sufficient, and the excess of nitric acid expelled by heat. The mass is then treated with a little water, the solution of sulphate of bismuth filtered off from the sulphate of lead, the latter washed with water containing sulphuric acid, dried and ignited.

From the filtrate the teroxide of bismuth is precipitated by carbonate of ammonia in excess; the liquid is digested for some time to ensure the complete separation of the precipitate, which is then filtered off, washed, detached as far as possible from the filter, and ignited in a porcelain crucible, when it is converted into yellow teroxide of bismuth. The filter is incinerated separately.

Bismuth and lead may be converted into sulphates, and separated in the same manner, when they are the sole constituents of the alloy.

45. SCHWEINFURT GREEN.

CuO, $\overline{A} + 3$ (CuO, AsO₃).

When this substance is heated with caustic potassa, the acids are extracted, and red suboxide of copper left, $\frac{1}{3}$ of the arsenious acid being converted into arsenic acid.

If the filtered liquid be neutralized with nitric acid, and nitrate of silver gradually added, a red-brown precipitate of arseniate of silver is first produced, and afterwards a yellow precipitate of arsenite of silver.

In order to separate the two acids, the solution, previously acidified with nitric acid, is mixed with excess of ammonia, and sulphate of magnesia added, which has been mixed with so much chloride of ammonium that it is no longer precipitated by ammonia. The arsenic acid is thus precipitated as arseniate of magnesia-ammonia. After the lapse of twelve hours, the precipitate is collected upon a dried and weighed filter, washed with dilute ammonia, and thoroughly dried at 100°. It then has the composition 2 MgO, NH₄O, AsO₅+HO, and contains 62·9 per cent of arsenic acid.—It is not safe to ignite this precipitate, since arsenic is then liable to be reduced and volatilized.

The solution filtered from the magnesia-precipitate is acidified with hydrochloric acid, and the arsenious acid precipitated as tersulphide of arsenic.

If the original pigment be digested with a mixture of concentrated hydrochloric acid and alcohol, a solution of chloride of copper is obtained, and the arsenious acid remains behind as a white powder.

By long digestion with an excess of sulphide of ammonium, the copper is separated as sulphide, while all the

arsenic is dissolved and may be precipitated as tersulphide of arsenic by adding hydrochloric acid to the filtrate.

When Schweinfurt green is distilled with dilute sulphuric acid, the acetic acid passes over, and may be converted into acetate of baryta by adding that base. The accurate quantitative estimation of the acetic acid can only be effected by ultimate organic analysis.

46. ARSENIC AND LEAD.

The alloy, in a fine state of division, is oxidized with nitric acid, the excess of acid evaporated, the solution neutralized with ammonia, and the precipitated white mass digested for some time with an excess of sulphide of ammonium in a closed vessel. The solution of sulphide of arsenic is filtered from the sulphide of lead, which is collected upon a weighed filter, washed, first with weak sulphide of ammonium, then with water, dried and weighed.

The sulphide of arsenic is precipitated from the solution by dilute hydrochloric acid, the sulphuretted hydrogen expelled by a gentle heat, the precipitate filtered off, washed, and gently heated, together with the filter, in a beaker, with concentrated hydrochloric acid, with gradual addition of chlorate of potassa, until all the arsenic and part of the sulphur are oxidized and dissolved. The solution is diluted with water, passed through a filter, which must be well washed, and the arsenic acid precipitated, as in No. 45, with sulphate of magnesia and ammonia.

47. ARSENIC AND TIN.

The following is the best method for the separation of these two metals from each other:

The finely-divided compound is gradually and carefully oxidized with nitric acid, which is dropped upon it in a weighed vessel. When it is converted into a dry white mass, more nitric acid is added, and the whole evaporated to perfect dryness in a water-bath. The mass dried at 100° is weighed. A portion of it is then weighed in a bulb-tube, one limb of which is bent downwards, and dips into caustic ammonia contained in a small flask. A stream of sulphuretted hydrogen is passed through the bulb-tube, and when it is filled with gas, the mass is heated, gently at first, afterwards more strongly, until a sublimation takes place of sulphide of arsenic and sulphur, which dissolve in the ammonia. When no fresh sublimate is formed, the apparatus is allowed to cool, and the piece of tube cut off in which any sublimate still remains. This tube is placed in warm solution of potassa, which easily dissolves the sublimate, the solution added to the sulphide of ammonium, and the whole liquid carefully acidified with hydrochloric acid which precipitates the sulphide of arsenic. Some powdered chlorate of potassa is added to the liquid, without filtering, and heat applied till there remains only pure sulphur, which is filtered off. From the filtrate, the arsenic acid is then precipitated by ammonia and sulphate of magnesia as in No. 45.

All the tin is left in the bulb in the form of dark brown bisulphide of tin, mixed, however, with a variable quantity of sulphur, so that the amount of tin cannot be immediately inferred from the weight of the residue. In order to determine the tin, the contents of the bulb are thrown into a porcelain crucible, moistened with nitric acid, and ignited, with access of air, until the tin is entirely converted into white binoxide, which is then weighed. The quantities of tin and arsenic are afterwards calcu-

lated for the whole quantity of the original oxidized mass.

Another method of analyzing the arseniferous tin consists in fusing it, in a finely-divided state, with 5 times its weight of carbonate of soda, and the same quantity of sulphur, in a porcelain crucible over a spirit-lamp; the fused mass is then dissolved in water, and the two sulphides precipitated from the very diluted solution by dilute hydrochloric acid. When all the sulphuretted hydrogen has been expelled by a gentle heat, the reddish-brown precipitate is thrown upon a weighed filter, washed, and dried at 100°; a weighed quantity of it is then heated, as directed above, in a stream of sulphuretted hydrogen.

48. TARTAR-EMETIC.

KO, SbO₃ $\bar{T} + 2$ HO.

The powdered salt loses all its water at 100°.

The substance is dissolved in about 300 times its weight of warm water, and the solution saturated with sulphuretted hydrogen. Some hydrochloric acid is afterwards added to promote the separation of the tersulphide of antimony; when the liquid has become clear, the precipitate is collected upon a weighed filter, well washed, dried at 150°, and weighed. In this case, the weight of the antimony may be at once inferred from that of the precipitate.

The filtrate is evaporated to dryness, the saline residue heated till the tartaric acid is completely carbonized, the carbonaceous mass digested with dilute hydrochloric acid, filtered off and thoroughly washed. The solution is evaporated, and the residual chloride of potassium gently ignited in a covered crucible, and weighed.

The amount of the tartaric acid is inferred from the difference. It can be directly determined only by ultimate organic analysis.

49. ANTIMONY AND LEAD.

The finely-divided compound is oxidized with nitric acid, the solution mixed with ammonia in slight excess, and afterwards with an excess of yellow sulphide of ammonium, with which it is digested for some time until the precipitate is perfectly black. The solution is then diluted with water, the sulphide of lead collected upon a dried and weighed filter, thoroughly washed with dilute sulphide of ammonium, and afterwards with water, dried at 150°, and weighed.

The sulphide of antimony is precipitated from the solution by dilute sulphuric acid, and the liquid exposed to the air until most of the sulphuretted hydrogen has been dissipated. The precipitate is then thrown upon a dried and weighed filter, well washed, and dried at 100° till its weight is constant.

Since the quantitative composition of this precipitate is not accurately known, and since, moreover, it contains some free sulphur, it must now be analyzed, and either the sulphur or the antimony in it determined.

To determine the amount of sulphur which it contains, a weighed quantity is detached from the filter and oxidized, very gradually and cautiously, in a flask, with concentrated nitric acid. Concentrated hydrochloric acid is afterwards added, and the mixture digested until all the antimony is

dissolved. As soon as this is the case, so much tartaric acid is added, that the solution may be diluted with water without any precipitation taking place. If any sulphur should have been separated in an unoxidized state, it must be collected upon a weighed filter. The sulphuric acid is then precipitated from the diluted solution by chloride of barium, and the precipitate washed with hot water. The quantity of sulphur, and, in consequence, that of the antimony, are calculated for the total weight of the precipitated sulphide of antimony.

For the direct estimation of the antimony, a weighed portion of the original precipitate is introduced into a weighed bulb-tube, and heated in a stream of hydrogen-gas, at first very gently, and ultimately to the fusing-point of the antimony, from which the sulphur is thus completely separated.

Or, instead of the hydrogen, a stream of carbonic acid gas may be passed through the tube, and the precipitate heated in it until it does not lose any more sulphur, and is converted into black tersulphide of antimony.

50. BOURNONITE.

$3 \text{ Cu}_2\text{S}, \text{SbS}_3 + 2 (3 \text{ PbS}, \text{SbS}_3).$

The powdered mineral is gradually and carefully oxidized with concentrated nitric acid, the mass mixed with ammonia, and digested for some time, in a closed vessel, with yellow sulphide of ammonium. The solution is then treated as directed in No. 49.

The residue containing sulphide of copper and sulphide of lead is dried in the funnel, detached, as far as possible, from the filter, the latter incinerated, and the sulphides afterwards oxidized, in a dish, by the gradual addition of fuming nitric acid. Some sulphuric acid is then added, the whole of the nitric acid expelled by heat, and the sulphate of copper extracted from the mass by water. The sulphate of lead is washed, dried and ignited. The oxide of copper is precipitated from the solution by caustic potassa, at a boiling heat.

This method is not quite accurate, since a little sulphide of copper dissolves in the sulphide of ammonium together with the tersulphide of antimony; sulphate of lead, moreover, is not quite insoluble. The determination of the lead is more accurate if all free sulphuric acid be expelled by heat before

the sulphate of copper is extracted with water.

A more exact method for the analysis of this mineral is that with chlorine, described in the article upon Fahlore.

51. ZINKENITE.*

PbS, SbS₃.

The amount of sulphur present may be inferred from the loss which the compound suffers when heated in a bulbtube, through which a stream of hydrogen is passed, when all the sulphur is evolved as sulphuretted hydrogen, and PbSb remains behind.

The relative proportions of lead and antimony are determined as in No. 49.

For the direct estimation of the sulphur, the finely-

* Plagionite, jamesonite, and feather-ore, are similar combinations. Zinkenite may be easily prepared artificially by fusing together 7½ parts of sulphide of lead, with 11 parts of black tersulphide of antimony in a glass tube.

divided compound is mixed with 3 parts of chlorate of potassa, and 3 parts of carbonate of soda, and heated, in a platinum crucible, at first gently, and ultimately to redness, until the chlorate of potassa is completely decomposed. The salts are then extracted from the mass with water, the residue well washed, the solution acidified slightly with hydrochloric acid, and the sulphuric acid precipitated by chloride of barium.

52. BERTHIERITE.

FeS, SbS3.

The mineral, in the state of fine powder, is oxidized with hydrochloric acid and chlorate of potassa, until the separated sulphur has a pure yellow colour. The solution is mixed with tartaric acid, and may then be diluted with water without any precipitation taking place. The separated sulphur is collected upon a dried filter, washed, and dried at 100°. The sulphuric acid produced by the oxidation is precipitated from the solution by chloride of barium, and the sulphate of baryta washed with hot water.

When the excess of baryta has been removed from the filtrate by sulphuric acid, a stream of sulphuretted hydrogen-gas is passed through the solution, and the antimony precipitated. (See also No. 49.)

From the filtered liquid the iron is precipitated by sulphide of ammonium. The mixture is digested for some time, and when the solution, which is at first tinged green by the fine particles of suspended precipitate, has at length become clear yellow, the precipitate is filtered off, washed

several times with solution of sulphuretted hydrogen from a wash-bottle, and dried in the funnel. The precipitate is then heated, together with the filter, in a porcelain crucible, until the paper is carbonized, then the iron dissolved out with aqua-regia, precipitated as sesquioxide by ammonia, ignited and weighed.

53. RED SILVER-ORE.*

Light-coloured, 3 AgS, AsS₃; dark, 3 AgS, SbS₃.

1. Dark.—To determine the amount of sulphur, a weighed quantity of the mineral is fused in a bulb-tube, over a large spirit-lamp or gas-burner, in a stream of dry hydrogen, as long as any sulphuretted hydrogen is formed; all the sulphur is thus expelled, in combination with hydrogen. The conclusion of the operation is also indicated by a sort of coruscation which takes place, and the antimonide of silver is left in the form of a perfectly bright, smooth, moveable globule.

The tube is allowed to cool slowly, weighed, and placed in communication with an apparatus for the evolution of chlorine, in a current of which the antimonide of silver

* These compounds may be readily obtained artificially by fusing their constituents together. That which contains antimony is prepared by fusing 46.5 parts of sulphide of silver with 22 parts of black tersulphide of antimony in a crucible, beneath a layer of common salt; to prepare the arseniferous compound, 23 parts of sulphide of silver and 7.5 parts of yellow tersulphide of arsenic, or 40.5 parts of powdered silver, 12 parts of sulphur, and 9.4 parts of arsenic are fused together in a glass tube closed at one end. Combination takes place with incandescence.

is fused, until no more pentachloride of antimony is volatilized, and pure fused chloride of silver remains. The latter is then treated as in the case of grey copper-ore.

The antimonide of silver may also be oxidized by nitric acid, and the silver and antimony separated by sulphide of ammonium, as in antimonide of lead (No. 49).

2. Light.—The light-coloured variety, when fused in a current of hydrogen, loses all its sulphur and arsenic; but the complete expulsion of the latter can scarcely be effected in a glass tube. The experiment must be conducted in a small porcelain boat, placed in a porcelain tube. After a certain time, the fused substance suddenly swells up to a voluminous bladder-like mass, from which the last portions of arsenic can be but slowly expelled.

The analysis may also be effected by dissolving the red silver-ore in concentrated nitric acid. The digestion is continued until the separated sulphur has a pure yellow colour; the solution is then diluted with hot water, and filtered from the sulphur, the total quantity of which may here be determined from the loss, unless it be directly determined, as in the case of copper-pyrites (No. 26); the silver is precipitated by diluted hydrochloric acid (see No. 1), the solution filtered off, concentrated by evaporation, with addition of some nitric acid or chlorate of potassa, and the arsenic acid precipitated by sulphate of magnesia and ammonia. (See No. 45.)

Or the very finely-powdered mineral may be fused with 5 times its weight of a mixture of equal parts of nitre and carbonate of soda in a platinum crucible, at the bottom of which a layer of carbonate of soda has been placed. The mass is afterwards dissolved out with hot water, the silver filtered off, washed, ignited and weighed. The solution is acidified with hydrochloric acid, mixed with

ammonia, and the arsenic acid precipitated by sulphate of magnesia. The amount of sulphur is determined by loss, unless it be precipitated from the original solution in the form of sulphate of baryta, when it must be very carefully washed with hot water to free it from the nitrate of baryta which it carries down.

Both compounds may also be analyzed with great accuracy by means of chlorine gas, as described in the article upon Grey Copper-ore.

In analyzing a mixture of light and dark red silver-ore, the arsenic and antimony are separated according to the method described in No. 55.

54. TIN AND ANTIMONY.

The weighed compound is dissolved in hydrochloric acid, with gradual addition of nitric acid, and a piece of pure tin placed in the solution, with which it is heated for some time, until the whole of the antimony is precipitated; the latter is collected upon a weighed filter, washed, dried at 100°, and weighed; the amount of tin is inferred from the difference.

In order to determine both metals directly, the compound, as finely divided as possible, is oxidized in a beaker with strong pure nitric acid, the mass evaporated to dryness, gently ignited, and fused, in a silver crucible, with a large excess of hydrate of soda. When cool, the mass is treated with water, rinsed out into a beaker, and the solution mixed with $\frac{1}{3}$ its volume of strong alcohol. The insoluble antimoniate of soda is thus separated from the stannate, carbonate, and excess of hydrate of soda, which are dissolved

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by the weak spirit. When the liquid has become perfectly clear, the precipitate is filtered off, and washed, first with a mixture of equal volumes of alcohol and water, and finally with strong alcohol.

The alkaline solution is heated to expel the alcohol, diluted with water, acidified with dilute sulphuric acid, and the tin precipitated by sulphuretted hydrogen. The bisulphide of tin is then converted into binoxide of tin, as directed in No. 44.

The antimonate of soda is detached as far as possible from the filter, and a mixture of hydrochloric and tartaric acids poured over the latter, and allowed to flow into the beaker containing the remainder of the precipitate. When the salt is perfectly dissolved, and the filter has been washed, the antimony is precipitated by sulphuretted hydrogen. The antimony contained in the precipitate is determined as in No. 49.

The antimonate of soda may also be collected upon a weighed filter, dried at 100°, and a weighed portion mixed with sal-ammoniac in a porcelain crucible, and ignited, when all the antimony is volatilized, and the salt converted into chloride of sodium. The operation must be repeated several times till the weight is constant, and the amount of the antimony may be calculated from that of the chloride of sodium obtained.

55. ARSENIC AND ANTIMONY.

If only these two metals be present, as in native arsenic, a complete separation may be effected by heating the compound in a bulb-tube through which a stream of dry carbonic acid gas is transmitted, when the whole of the arsenic is volatilized, and the antimony remains behind. If too strong a heat be applied, a portion of the latter metal may also be volatilized.

When the compound under examination contains, as is often the case, the two metals in the form of sulphides, they may be at least approximately separated by digestion with concentrated hydrochloric acid, which dissolves the sulphide of antimony, and leaves that of arsenic. When the latter has a pure yellow colour, the solution is mixed with tartaric acid, diluted with water, and the sulphide of arsenic filtered off and washed. It is afterwards oxidized with hydrochloric acid and chlorate of potassa, and the arsenic acid precipitated by sulphate of magnesia and ammonia. (See No. 45.)

Or the two sulphides may be mixed with 6 times their weight of a mixture of 4 parts of nitrate and 2 parts of carbonate of soda, and the mass gradually heated in a silver crucible until perfectly white; it is then digested with water, which leaves the antimony undissolved as antimonate of soda; this is filtered off, washed with weak spirit, and weighed; its composition is NaO, SbO₅. By repeated ignition with sal-ammoniac, all the antimony may be volatilized, and the salt converted into chloride of sodium.

The solution, which contains the arsenate of soda together with the other salts, is acidified with nitric acid, mixed with ammonia, and the arsenic acid precipitated by sulphate of magnesia.

The most accurate method of separation is as follows: The compound is carefully oxidized with aqua-regia, or with hydrochloric acid and chlorate of potassa, some tartaric acid and a considerable quantity of chloride of am-

monium added, and the mixture then treated with ammonia in excess, which must dissolve the whole. From this solution the arsenic acid is precipitated by sulphate of magnesia. (See No. 45.)

The filtrate is acidulated with hydrochloric acid, and the antimony precipitated by sulphuretted hydrogen.

Or the compound containing arsenic and antimony is oxidized with aqua-regia, or with hydrochloric acid and chlorate of potassa; and if any other metals precipitable by sulphuretted hydrogen be present, the mass is neutralized with ammonia, and digested with an excess of yellow sulphide of ammonium to extract the arsenic and antimony. These are precipitated from the filtered solution by dilute sulphuric acid, collected upon a weighed filter, and dried at 100°.

If, however, no other metals precipitable by sulphuretted hydrogen be present, the solution in aqua-regia is mixed with tartaric acid, diluted with water, heated to 60°, and the arsenic and antimony precipitated by sulphuretted hydrogen. The solution, through which the gas is passed until it has cooled, is allowed to stand in a covered vessel for at least twenty-four hours; the excess of gas is then allowed to pass off, the precipitate collected upon a weighed filter, washed, dried at 100°, and weighed.

A weighed portion of the precipitate is then thrown into a beaker, and treated with concentrated hydrochloric acid, in which some chlorate of potassa has been previously dissolved by the aid of a gentle heat; more chlorate of potassa is added, until all the unoxidized sulphur has separated with a pure yellow colour. The mass is then mixed with tartaric acid, diluted with water, and the sulphur collected upon a dried filter and weighed. From the filtrate the sulphuric acid is precipitated by

chloride of barium, and the amount of sulphur, calculated from the weight of the sulphate of baryta, is added to that previously obtained.

Another portion of the sulphuretted hydrogen precipitate is weighed in a bulb-tube, and heated in a stream of hydrogen, when all the sulphur and arsenic are carried off, and there remains only the antimony, which is weighed after the sublimate of arsenic and sulphide of arsenic has been expelled from the tube by gently heating in the stream of hydrogen; the amount of arsenic is inferred from the difference. The results are calculated for the whole weight of the precipitate produced by sulphuretted hydrogen.

Lastly, antimony and arsenic may also be separated by mixing the dry sulphides intimately with 12 times their weight of a mass consisting of 3 parts of dry carbonate of soda, and 1 part of cyanide of potassium. This mixture is heated in a bulb-tube in a slow current of dry carbonic acid, when the whole of the arsenic is reduced and sublimes as a metallic mirror, whilst the antimony remains in the mass.

56. ARSENIC, ANTIMONY, AND TIN.

The compound is divided as finely as possible, and carefully oxidized with strong and pure nitric acid, the mass evaporated to dryness and fused in a silver crucible with 8 times its weight of hydrate of soda, the evaporating vessel being previously rinsed with solution of soda, which is added to the contents of the crucible and evaporated to dryness. The fused mass is treated with hot water, then diluted with water, and $\frac{1}{3}$ its volume of strong alcohol

added. The mass is allowed to stand for twenty-four hours and frequently stirred; the antimonate of soda is then filtered off, and washed first with a mixture of 2 vols. of water and 1 vol. of alcohol, next with a mixture of equal vols., and lastly with a mixture of 3 vols. of alcohol and 1 vol. of water, adding to each a few drops of solution of carbonate of soda. The washed salt is treated as in No. 54.

The alkaline filtrate is supersaturated with hydrochloric acid, which produces a bulky precipitate of arsenate of binoxide of tin. Without filtering this off, the liquor is saturated with sulphuretted hydrogen, the precipitate thus converted into a dark brown mixture of bisulphide of tin and tersulphide of arsenic, and the liquor then allowed to stand for twenty-four hours in the closed vessel. The precipitate is now collected on a weighed filter and dried at 100°. The separation of the tin and arsenic is effected by heating in sulphuretted hydrogen, as in No. 47.

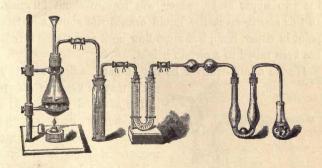
A weighed portion of the entire precipitate might also be mixed with about 12 times its weight of a mixture of 3 parts of carbonate of soda and 1 part of cyanide of potassium, and heated in a covered porcelain crucible until all the arsenic is driven off. On treating the residue with water, the tin would be left behind in the metallic state.—Or the mixture could be heated in a long glass tube, in a slow current of carbonic acid gas, and thus the arsenic obtained as a sublimate in the tube. In order to secure a more complete condensation, a weighed coil of fine sheet copper could be introduced into the tube, and heated to ignition at one place for the purpose of forming arsenide of copper.

57. FAHL-ORE.

4 (CuS, AgS, FeS, ZnS, HgS), (SbS₃, AsS₃).

Every specimen of fahl-ore does not contain all these constituents; some of them may be entirely absent, and generally they may replace each other in the different kinds in varying quantities.

The analysis is best effected by gently heating the mineral in dried chlorine gas, when sulphur, arsenic, antimony, mercury, and a portion of the iron are volatilized in the form of chlorides, and copper, silver, zinc and part of the iron remain behind, likewise converted into chlorides.



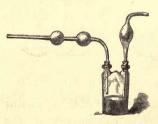
The above figure shows the construction of the apparatus to be used in such analyses. The chlorine gas, for the purpose of drying it, is first passed through a small cylinder containing concentrated sulphuric acid, and thence through the chloride-of-calcium-tube, which is fixed upon a wooden stand.

The mineral, finely divided, is weighed in the bulb-tube. The latter is best provided with two bulbs, in order to collect the greater portion of the sublimate in the second bulb, and thus to prevent the tube from being stopped up.

The end of the tube bent downwards is connected by means of a good cork or a caoutchouc tube, with the three-bulb-tube or receiver, in which the volatile products are to be condensed. The other end of the latter is provided with a small conducting-tube, through which the excess of chlorine passes into a small flask containing alcohol, or milk of lime.

In order to prevent the precipitation of antimony, the three-bulb receiver is not filled with pure water, but with a mixture of dilute hydrochloric and tartaric acids, whenever that substance is present; the liquid should fill about \(\frac{1}{3}\) of the two upper bulbs, which will require about 50 grms. In this arrangement the liquid cannot rise above a certain point in either limb, but must flow back again whenever it has been raised to a certain height.

If such a bulb-receiver be not at hand, a flask with two



necks may be used, as shown in the annexed figure. The perpendicular limb of the bulb-tube almost touches the mixture of acids in the receiver, but does not dip into it, because the liquor might in that case recede into the

bulb-tube, the chlorine being rapidly absorbed. The conducting-tube, inserted through the second neck, expands at its upper portion into a bulb, and is cut off below in an oblique direction; it enters the liquid so far, that this can

be pressed up into the bulb only, and must then flow back again. To this tube a second one is attached, which is bent at a right angle, and conducts the excess of chlorine into alcohol, or milk of lime.

It is advisable not to connect the bulb-tube, containing the mineral, with the chlorine apparatus, until most of the atmospheric air has been expelled from it.

The complete decomposition of the fahl-ore takes place even at the ordinary temperature, with strong evolution of heat. When the bulb has nearly cooled again, it is heated by a very small spirit-lamp-flame, in order to separate the volatile products from the non-volatile, and to drive the former into the second bulb. It is scarcely possible to drive off all the sesquichloride of iron; the heating is therefore discontinued as soon as vapours of this compound only appear to be evolved.

The chlorine gas is to be passed through in a gentle current only, especially towards the last, when the sublimation is effected, because otherwise the vapours of the volatile products may pass unabsorbed through the receiver.

When the tube has become clear between the bulbs, and the apparatus has cooled, it is cut through between the bulbs by means of a file and a red-hot coal, and the end with the bulb containing the sublimate is covered with a short, glass tube, sealed at one end and moistened with water on the inside. The tubes are allowed to remain connected in this manner for at least twenty-four hours, in order to cause the sublimate gradually to attract moisture and to prevent its becoming hot and thus occasioning loss on being afterwards dissolved in water, as would otherwise be the case. It is then dissolved in a little water, to which some hydrochloric and tartaric acids have been added, the tube is carefully rinsed, and the

rinsings added to the solution in the receiver. Should the liquid be cloudy, in consequence of a separation of antimonious acid, a gentle heat must be applied, in order to redissolve the latter. In case of sulphur having separated in an unoxidized state, it must be filtered off.

I. Analysis of the Fixed Residue.—The bulb containing it is placed in a beaker with dilute hydrochloric acid, and digested until the contents are dissolved, with the exception of the chloride of silver. This is filtered off and treated as in No. 1. Should chloride of lead be present, as is the case in the analysis of bournonite, it must be dissolved by using a larger quantity of water. In this case the contents of the bulb have to be heated very cautiously, that the chloride of lead may not volatilize.

A slow current of sulphuretted hydrogen is then passed through the solution until it is completely saturated. The precipitated sulphide of copper is treated as in No. 25, or if lead be present, as in No. 50.

The solution filtered off from the precipitate contains part of the iron, and if too great a heat was avoided, all the zinc; it is then heated to ebullition, and mixed with some chlorate or hypochlorite of an alkali, in order to convert the former metal into a higher oxide; the iron and zinc are then separated and determined as in No. 27.

II. ANALYSIS OF THE VOLATILE PRODUCTS.—This solution contains the mercury, antimony, arsenic, a portion of the iron, and the sulphur, partly in the form of sulphuric acid, partly unoxidized.

The sulphuric acid can be precipitated with chloride of barium, and the excess of baryta again removed by sulphuric acid.

It is, however, much more convenient to determine the amount of sulphur in a separate portion of the mineral.

For this purpose it is finely divided, mixed with 3 times its weight of finely-powdered chlorate of potassa and then with as much of dry carbonate of soda, and the mixture very gradually heated in a platinum crucible (the bottom of which is previously covered with carbonate of soda, as a precaution) until all the chlorate of potassa is decomposed. When cold, the mass is treated with water, the solution filtered, slightly acidulated with hydrochloric acid, and the sulphuric acid precipitated by chloride of barium as in No. 3.

For the determination of the other constituents, the solution of the volatile chlorides is heated to about 60° and then a gentle current of sulphuretted hydrogen passed through it until it is cold. When completely saturated with sulphuretted hydrogen, the solution is allowed to stand for twelve hours, and then the precipitate, which consists of the sulphides of mercury, antimony and arsenic, collected on a filter which has been dried and weighed. After being washed with sulphuretted-hydrogen-water, the precipitate is removed from the filter, taking care not to damage the latter; it is washed off as well as possible, and a concentrated solution of sulphide of ammonium poured upon it, with which it is digested in a closed vessel until the whole of the sulphides of arsenic and antimony are dissolved, and the sulphide of mercury has assumed a pure black colour. When completely cold, it is again collected on the filter previously used, washed first with dilute sulphide of ammonium, and towards the end with pure water, dried and weighed.

From the solution in sulphide of ammonium, the sulphides of arsenic and antimony are precipitated by an excess of dilute sulphuric acid, and separated and determined as in No. 55.

From the liquid which has been filtered off from the precipitate by sulphuretted hydrogen, the iron can only be separated by sulphide of ammonium after neutralizing with ammonia, on account of the presence of tartaric acid. When the sulphide of iron is completely separated by digestion at a gentle heat, it is filtered off, and washed with sulphuretted-hydrogen-water; the filter is then put into a beaker, and digested with hydrochloric acid until all the sulphide of iron is dissolved. The solution is then filtered off from the paper, the latter washed, the liquid heated with chlorate of potassa, and the sesquioxide of iron precipitated by ammonia.

If the amount of sulphide of iron be but small, the filter is ignited with the precipitate, the air having free access, until all the iron is converted into sesquioxide, and its weight remains constant.

58. GERMAN SILVER (ARGENTAN).

(Cu, Ni, Zn).

The alloy is dissolved in nitric acid, the greater excess of acid evaporated, the solution diluted with water, and the copper precipitated by means of sulphuretted hydrogen (see No. 25).

The filtered liquor is concentrated by evaporation, precipitated by an excess of solution of potassa, and heated with it, when the protoxide of nickel is separated and the oxide of zinc dissolved. From this solution the latter is precipitated by sulphide of potassium, or, after being saturated with hydrochloric acid, by carbonate of soda at a boiling heat.

In this manner, however, the oxides of nickel and zinc

cannot be separated with precision; some oxide of zinc remains with the protoxide of nickel.

The separation is also effected incompletely by fusing the mixture of the oxides with hydrated potassa, or by precipitating both oxides with carbonate of soda at a boiling heat, converting the protoxide of nickel into black sesquioxide by digestion with hypochlorite of soda, and then extracting the oxide of zinc by means of caustic potassa.

I. More accurate results are obtained by igniting the dried mixture of both oxides, reducing it to a fine powder and heating it in a current of dry oxygen as long as water is formed. From the mixture of nickel and oxide of zinc the latter is then extracted by digestion for a somewhat long period with a concentrated solution of carbonate of ammonia, air being excluded.

II. Or the oxides precipitated from the hot solution by carbonate of soda are dissolved in acetic acid, the solution mixed with a considerable quantity of free acetic acid, and sulphuretted hydrogen passed through it, very gradually and with continued agitation of the liquid, as long as the precipitate remains white, when only zinc is precipitated. The hydrochloric or nitric solution can also be mixed with an excess of acetate of soda, and the zinc precipitated by sulphuretted hydrogen.

III. The precipitated oxides are mixed with 3 parts of carbonate of potassa and as much sulphur, the mass carefully heated in a porcelain crucible to tranquil fusion, and on cooling, the alkaline sulphide extracted with water. The metallic sulphides remaining behind are then treated with dilute hydrochloric acid, which dissolves only the sulphide of zinc.

59. COPPER-NICKEL.*

Ni₂ As.

I. Preparation of Pure Nickel.—A mixture of 1 part of very finely-powdered arsenide of nickel, 2 parts of nitrate of potassa, and 2 parts of carbonate of potassa, is ignited for a considerable period, and all the arsenate of potassa extracted from the mass by means of water.

Or the arsenide of nickel is fused with 3 times its weight of sulphur and carbonate of potassa, and the sulph-arsenate of sulphide of potassium thus formed, extracted with water.

The mixture of oxides remaining behind in the first case, is dissolved in hydrochloric acid, that of the sulphides, in the second case, in hydrochloric acid with gradual addition of nitric acid and with application of heat.

The solution is heated to about 70°, and during that time, and until it has cooled, saturated with sulphuretted hydrogen; it is then allowed to stand in a closed vessel for twenty-four hours, when copper, bismuth, and a residue of arsenic are precipitated.

The sulphuretted hydrogen having been expelled by heat, the solution is filtered, heated to boiling, and precipitated by carbonate of soda; the precipitate, containing all the nickel, cobalt, and iron, is thoroughly washed.

It is then, whilst still moist, treated and digested with an excess of a hot saturated solution of oxalic acid, when all the iron is dissolved, and the nickel and cobalt are left in the form of oxalates. They are filtered off, washed, and

* Arsenide of nickel, with a varying amount of cobalt and iron. The smelting-products, known by the name of cobalt- and nickelspeiss, have a similar composition, and contain besides frequently accidental admixtures of copper and bismuth.

digested with concentrated caustic ammonia until they are dissolved.

The blue solution is then set aside in an open vessel until all the free ammonia has evaporated, during which time the nickel separates in the form of green oxalate of protoxide of nickel and ammonia, whilst the cobalt remains in the solution to which it imparts a red colour.

The nickel-salt is filtered off, washed, and ignited in a closed crucible or in a glass tube, when pure metallic nickel remains behind.

The cobalt may be obtained from the solution by evaporation and ignition of the residue, or by boiling it with caustic potassa until no farther disengagement of ammonia takes place; or when smaller quantities are operated upon, by an alkaline sulphide, and subsequent addition of dilute sulphuric acid in order to separate the sulphide of cobalt.

The pure metal may be easily prepared from commercial nickel by dissolving it in hydrochloric acid with the addition of some nitric acid, purifying the solution by sulphuretted hydrogen, and then precipitating nickel and cobalt by the addition of a boiling saturated solution of binoxalate of potassa. The washed precipitate is then dissolved in ammonia.

For the purpose of separating the iron, the solution, after being again oxidized, may also be mixed with chloride of ammonium, and then with ammonia in excess, when sesquioxide of iron (with a little nickel and cobalt) is precipitated, whilst nickel and cobalt remain in solution. Or the solution is neutralized with carbonate of soda, mixed with acetate of soda, and boiled, when sesquioxide of iron is precipitated.

II. QUANTITATIVE ANALYSIS.—The very finely-powdered

arsenide of nickel is fused with $2\frac{1}{2}$ parts of nitrate of potassa and 3 parts of carbonate of soda, in a platinum crucible, the bottom of which has previously been covered with carbonate of soda; the mass is then ignited for some time, and when cold is digested with water; the oxides formed are filtered off and washed.

I. The solution contains all the arsenic in the form of arsenates of the alkalies; it is supersaturated with hydrochloric acid, then evaporated almost to dryness, in order to expel the nitric acid, the mass dissolved in water, and heated to about 70°, while sulphuretted hydrogen is passed through it. When the precipitation of sulphide of arsenic appears to be completed, the whole is allowed to cool, whilst the current of sulphuretted hydrogen is still passing.

The liquid is then left to stand in a closed vessel for twenty-four hours, the precipitate collected on a filter (which has previously been dried at 100° and weighed), washed, dried at 100° and weighed.

The precipitate is usually a mixture of AsS₃ and sulphur. A small portion of it is taken, weighed, and completely oxidized by heating it with aqua-regia or with hydrochloric acid and chlorate of potassa. From the solution diluted with water, the sulphuric acid formed is precipitated by chloride of barium, and from the quantity of sulphate of baryta the amount of sulphur calculated, and consequently also that of the arsenic, the amount found being afterwards calculated for the whole quantity of the precipitate.

It is more convenient, and quite as exact, to precipitate the arsenic acid from the alkaline solution in the form of arsenate of ammonia and magnesia. The solution is saturated with hydrochloric acid, mixed first with solution of chloride of ammonium, then with concentrated caustic ammonia, and lastly with sulphate of magnesia. After

twenty-four hours the precipitate is collected on a weighed filter, washed with dilute caustic ammonia, dried at 100° and weighed (see No. 45).

The arsenic may also be determined from the loss.

II. The oxides are dissolved in concentrated hydrochloric acid, and the copper and bismuth precipitated from the solution by sulphuretted hydrogen. The precipitate is treated as in No. 64.

III. The liquid filtered off from the precipitate is heated nearly to boiling, and mixed with some chlorate of potassa in order to peroxidize the iron, which may then be separated from the nickel and cobalt in the same manner as from manganese, either by succinate of ammonia or by carbonate of baryta (see No. 23).

From the liquid filtered off from the succinate of iron, nickel and cobalt are precipitated at a boiling-heat by caustic potassa, filtered off, and washed with hot water.

From the liquid separated from the carbonate of baryta, the dissolved baryta is precipitated by sulphuric acid, and the nickel and cobalt are then precipitated from the hot solution by caustic potassa.

IV. The precipitate containing the hydrated oxides of nickel and cobalt is gradually mixed, whilst still moist, with dilute hydrocyanic acid and solution of potassa (cyanide of potassium), and a gentle heat applied until it is dissolved. The yellowish-red solution is heated to boiling, in order to expel the excess of the hydrocyanic acid and to convert the cyanide of cobalt and potassium into the cobalticyanide, and is then mixed, whilst still warm, with levigated protoxide of mercury. By this treatment the cyanide of nickel and potassium is decomposed and all the nickel precipitated, partly in the form of oxide, partly as cyanide, whilst mercury takes its place.

The precipitate, when washed and ignited with access of air, leaves pure oxide of nickel behind.

If the mixture of both oxides, previously to the treatment with hydrocyanic acid and potassa, have been dried and reduced to metal by igniting it in a current of hydrogen (and the metal weighed), the amount of cobalt need not now be determined directly.

If this be not the case, the solution which still contains the cobalt is carefully neutralized with nitric acid, and solution of nitrate of suboxide of mercury, as neutral as possible, added, as long as it produces a precipitate of cobalticyanide of mercury. After being washed and dried, the precipitate is ignited with access of air, when it is converted into black oxide of cobalt, which, after being weighed, must be reduced by strong ignition in a current of hydrogen, on account of its amount of oxygen varying according to the temperature.

When the nickel-speiss contains lead and sulphur, the same method is used which has been given for the analysis of the fahl-ores, where the compound is decomposed by heating it in a current of dry chlorine-gas.

60. SPEISS COBALT.*

CoAs.

The analysis and the preparation of pure cobalt can be effected by the same process as the analysis of copper-nickel and the preparation of pure nickel. The following modifications facilitate the preparation:

I. Since the arsenide of cobalt contains upwards of 70

^{*} Arsenide of cobalt, with small quantities of nickel, iron and copper.

per cent of arsenic, it is advisable to remove a great portion of it by roasting. This is done by exposing it, finely powdered and in a thin layer, to a gentle red heat, in a crucible which is placed obliquely in the fire under a chimney with a good draught, and continuing the operation as long as vapours of arsenic escape. The roasted mass is then dissolved, with the aid of heat, in concentrated hydrochloric acid, to which some nitric acid or chlorate of potassa has been added.

II. From the dilute solution all the sesquioxide of iron (with a portion of the arsenic acid) can be removed by the careful addition of carbonate of soda.

III. On mixing the solution, which should contain all the arsenic in the form of arsenic acid, with a sufficient quantity of sesquichloride of iron, neutralizing with carbonate of soda, and then adding acetate of soda in excess, and boiling, all the arsenic acid is precipitated along with the entire quantity of iron. The solution is then filtered, again acidulated with hydrochloric acid, and treated with sulphuretted hydrogen in order to remove those metals which are precipitated by that reagent (for instance, copper); cobalt and nickel are then precipitated at a boiling heat by means of caustic potassa.

IV. Or the solution mixed with hydrochloric acid is considerably concentrated by evaporation, mixed with salammoniac and ammonia in excess, and the brown solution allowed to stand exposed to the air until it has acquired a fine purple tint. If it be now saturated with hydrochloric acid and heated to boiling, the greater portion of the cobalt separates in the form of a carmine crystalline powder, which appears to be $2 \text{ CoNH}_2 + 3 \text{ NH}_4\text{Cl}$, and when ignited leaves protochloride of cobalt.

61. COBALT-GLANCE.

$CoS_2 + CoAs.$

I. The finely-powdered mineral is decomposed by heating it in a current of dry chlorine-gas, as in the analysis of the fahl-ores, when the cobalt remains behind in the form of protochloride, whilst arsenic and sulphur are obtained as acids, dissolved in the water of the receiver. The protochloride of cobalt can then immediately be reduced to metal, in the same tube, by heating it in hydrogen, and weighed, if the determination of the small amount of iron contained in it be neglected; or it is dissolved in water acidulated with hydrochloric acid, and the solution precipitated at a boiling heat by caustic potassa. The small amounts of nickel and iron contained in the oxide of cobalt are then determined as in No. 60.

The sulphuric acid is determined by means of chloride of barium, and the excess of baryta removed by sulphuric acid. The filtered solution is concentrated by evaporation, and the arsenic acid precipitated by sulphate of magnesia and ammonia as in No. 45.

II. The mineral is dissolved in concentrated hydrochloric acid, with gradual addition of nitric acid, until it is completely dissolved, or the undissolved sulphur is left behind with a fine yellow tint. The latter is then collected on a weighed filter, dried at 100° and weighed.

From the solution, the sulphuric acid is precipitated by chloride of barium, and the amount of sulphur calculated from the precipitate, is added to that directly determined.

The excess of baryta is removed from the solution by sulphuric acid.

The filtrate is mixed with sulphurous acid, allowed to

stand for twenty-four hours, then heated to boiling until the excess of sulphurous acid is completely driven off, and when cooled down to about 50°, saturated with sulphuretted hydrogen. Thus saturated, it is left to stand for twenty-four hours, the sulphuretted hydrogen removed by gentle evaporation, and the sulphide of arsenic collected on a weighed filter and dried at 100°. It is then treated as in No. 46.

The solution of cobalt filtered from this precipitate is heated to boiling, mixed with a little chlorate of potassa, in order to bring the iron to a higher state of oxidation, carefully neutralized with carbonate of soda, and the iron precipitated with succinate of soda as in No. 23.

The protoxide of cobalt is precipitated from the filtered solution at a boiling heat by means of caustic soda, washed with hot water, ignited, and reduced in a current of hydrogen at as high a temperature as possible. When moistened with water after being weighed, the metal must not exhibit an alkaline reaction.

III. One part of the very finely-powdered mineral is mixed with 3 parts of finely-powdered chlorate of potassa and 3 parts of dry carbonate of soda, and the mixture heated very gradually in a platinum crucible over a spirit-lamp until it is in a state of tranquil fusion. The mass is then treated with warm water and the black oxide of cobalt filtered off. The solution is slightly acidified with hydrochloric acid and the sulphuric acid precipitated by chloride of barium. After the excess of baryta has been removed by sulphuric acid, the solution is concentrated by evaporation, mixed with sal-ammoniac and sulphate of magnesia, and the arsenate of magnesia-ammonia precipitated by adding ammonia.

The oxide of cobalt is dried, the filter incinerated, the ash

added to the oxide, and the whole dissolved in concentrated hydrochloric acid. The sesquioxide of iron is then precipitated, by means of succinate of soda, from the dilute solution, after carefully neutralizing with carbonate of soda.

The sesquioxide of iron cannot be precipitated, in this case, by carbonate of baryta, because some oxide of cobalt is precipitated at the same time; neither does the precipitation by an excess of ammonia lead to exact results, on account of some oxide of cobalt remaining combined with the sesquioxide of iron.

An approximate separation of both oxides may also be effected by neutralizing the solution with ammonia, precipitating both metals by sulphide of ammonium, and then adding a slight excess of dilute hydrochloric acid, when sulphide of iron is dissolved and sulphide of cobalt is left undissolved.

Or both oxides are precipitated by caustic potassa, the precipitate washed, removed from the filter, and the latter carefully cleansed with water from the washing-bottle; the mass is then mixed with a slight excess of powdered oxalic acid, when the oxide of cobalt is converted into rose-coloured, insoluble oxalate, whilst the sesquioxide of iron is dissolved. After twenty-four hours the former is collected on a weighed filter, washed with cold water, dried at 100°, and a weighed portion of it ignited in a glass tube, one end of which is sealed, whilst the other is drawn out into a point; by this process the oxalate of cobalt is reduced to metal. Whilst the tube is still red-hot the point is sealed with the blow-pipe, and the tube weighed when cold.

62. MANGANESE AND COBALT, OR NICKEL.*

For the merely approximate separation, the oxides are precipitated by carbonate of soda, the precipitate dissolved in an excess of acetic acid and the cobalt or nickel precipitated from the solution by sulphuretted hydrogen, when manganese remains dissolved. The solution of the chlorides or of the sulphates may also be mixed with acetate of soda, and the nickel or cobalt precipitated by sulphuretted hydrogen.

A more accurate, but still not absolute separation, may be effected by neutralizing the solution of the chlorides with ammonia, precipitating the metals by sulphide of ammonium, and mixing the solution with an excess of very dilute hydrochloric acid, when the sulphide of manganese is dissolved with great facility, whilst the sulphides of nickel or cobalt remain undissolved.

This method of separation is perfectly exact if the sulphides be used which were formed at a high temperature. The oxides are precipitated at a boiling heat by carbonate or hydrate of soda, the precipitate ignited and weighed, and then heated to dull redness in a current of sulphuretted hydrogen, in a porcelain boat, placed in a porcelain tube. When cold, the porcelain boat is put into very dilute hydrochloric acid, which dissolves the manganese only, and leaves the sulphide of cobalt or nickel behind.—The conversion of the oxides into sulphides may likewise be effected

^{*} Black cobalt-ore (earthy ore of cobalt) is a compound of protoxide of cobalt with binoxide of manganese. Moreover, almost every variety of manganese-ore contains small quantities of cobalt for the detection of which the residues of the preparation of chlorine may be used.

by fusing them in a porcelain crucible with 3 times their weight of carbonate of soda and as much sulphur, after which the mass is treated with dilute hydrochloric acid.

The following method is likewise accurate: The acid solution is mixed with cyanide of potassium, when the cyanides of manganese and cobalt are precipitated. Cyanide of potasssium is then added in excess, which dissolves all the cyanide of cobalt and a portion of the cyanide of manganese. The undissolved cyanide of manganese is filtered off, washed, and ignited with access of air. The filtered liquor is heated to boiling, and a drop of hydrochloric acid added from time to time; the protocyanide of cobalt is thus converted into sesquicyanide. Hydrochloric acid is then added and the boiling continued until, on farther addition of acid, the odour of hydrocyanic acid is no longer perceptible. By this time the double cyanide of manganese is converted into chloride of manganese, and the manganese can now be precipitated from the hot solution by means of carbonate or hydrate of soda, whilst all the cobalt remains in solution in the form of cobalticyanide of potassium. The separation of the cobalt from this solution is effected as in No. 59.

63. METEORIC IRON.

Iron of meteoric origin can be recognized by the following peculiarities:

I. Some meteoric iron contains olivine which may be detected by the eye.

II. In certain kinds, especially on the oxidized surface, yellowish, pliable laminæ of a metallic lustre may be ob-

served; they are phosphide of nickel and iron (Schreibersite).

III. Some kinds are passive, i. e., they do not reduce copper from a solution of neutral sulphate of copper.

IV. If a freshly filed, ground and polished surface be immersed for five or ten minutes in dilute nitric acid, peculiar, mostly crystalline delineations (Widmannstätten's figures), or microscopic parallel lines or bright points, make their appearance in most kinds, thus imparting to the surface a peculiar lustre when viewed in a certain direction.

V. All meteoric iron, when dissolved in hydrochloric acid, leaves a black, pulverulent residue, whilst in most cases a trace of sulphuretted hydrogen is developed, derived from an admixture of sulphide of iron. On examining this residue (previously washed and dried) under a magnifying power of from 50 to 100, in most cases crystalline particles of metallic lustre, and frequently also well-defined magnetic prisms of metallic lustre, are observed, consisting of phosphide of iron, phosphide of iron and nickel, and sometimes also chrome-iron and graphite; in addition to these also transparent, partly colourless, partly coloured grains of quartz, olivine and other minerals.

VI. Every specimen of iron of undoubted meteoric origin contains as characteristic constituents, nickel, cobalt and phosphide of iron and nickel. The amount of nickel varies between 2 and 20 per cent; the cobalt rarely amounts to 1 per cent, and the insoluble residue usually amounts to 3 per cent.

In order to detect the nickel, the hydrochloric solution is first saturated with sulphuretted hydrogen in order to precipitate traces of copper and tin, which occasionally occur; the protochloride of iron is then converted into sesquichloride by heating the solution nearly to boiling, and adding small quantities of chlorate of potassa. The solution is then mixed with an excess of ammonia, when all the sesquioxide of iron is precipitated, whilst most of the nickel remains dissolved. When the amount of nickel is rather large, the filtered liquor is more or less blue. Sulphide of ammonium precipitates from it black sulphide of nickel.

In order to detect the phosphoric acid contained in the sesquioxide of iron, it is dried and ignited with an equal weight of carbonate of potassa and soda, and the alkaline phosphates extracted with water. The solution is then supersaturated with acid and the phosphoric acid precipitated by ammonia and sulphate of magnesia.

In order to obtain the amount of phosphorus contained in the black residue left on dissolving meteoric iron in hydrochloric acid, it is finely powdered, mixed with about half its weight of nitrate of potassa and then with an equal weight of carbonate of soda, and ignited; the mass is then extracted with water and treated as above. The oxidized residue is dissolved in hydrochloric acid and the nickel detected as above.

In quantitative analyses the iron is separated from the nickel and cobalt, either by succinate of ammonia, or by carbonate of baryta, see No. 23. Cobalt and nickel are separated by cyanide of potassium as in No. 59.

64. BISMUTH AND COPPER.

The solution of these two metals in an acid is mixed with carbonate of ammonia in excess, when the protoxide of copper remains in solution, whilst the teroxide of bismuth is precipitated; it is filtered off, but only after some time, washed with carbonate of ammonia, dried and ignited. See No. 44.

Or the solution of both metals is mixed first with caustic potassa in excess, and then with hydrocyanic acid (cyanide of potassium), when the copper is dissolved as double cyanide, whilst the oxide of bismuth is left undissolved. See No. 27.

When the two metals have been precipitated by means of sulphuretted hydrogen, the precipitate is washed with water containing sulphuretted hydrogen, dried on the funnel, removed from the filter as much as possible, the latter carefully incinerated, and the ash added to the precipitate; this is then oxidized and dissolved by strong nitric acid, with gradual addition of some sulphuric acid, and the solution treated as above.

65. PLATINUM-ORE.

(Platinum with small quantities of Iridium, Palladium, Rhodium, Osmium, Ruthenium, Iron and Copper.)

An accurate quantitative analysis of native platinum is very difficult and tedious. In order to determine, at least, the amount of platinum, the following method is used:

The real grains of platinum are first picked out and separated chiefly from the darker steel-coloured grains of osm-iridium. The magnetic grains are next picked out by means of a magnet; these, which contain a larger amount of iron, are to be analyzed by themselves.

Two to three grms. of the mineral are then dissolved, at a boiling heat, in a mixture of 5 parts of fuming hydrochloric acid and 1 part of fuming nitric acid, in a retort connected with a receiver which is to be kept perfectly

cold. The acid is distilled off until the contents of the retort have acquired the consistence of a syrup. The mass becomes solid on cooling; it is then dissolved in a small quantity of water and the clear solution carefully poured off from the residue. The acid which was distilled over, contains osmic acid and is coloured yellow by a portion of the solution which was mechanically carried over; it is poured back on the residue and again distilled, in order to complete the solution.

The distillate containing osmic acid may be saturated with ammonia and the osmium separated as in No. 66. Or it is nearly saturated with hydrate of lime, mixed with an alkaline formate and boiled, when the osmium is reduced as a bluish-black powder. Or the distillate is saturated with caustic potassa, some alcohol added, and gently heated, when osmite of potassa (KO, OsO₃) is precipitated in the form of a beautiful red crystalline powder. It is washed with alcohol, on account of its being soluble in water, and ignited in a current of hydrogen when the osmium is obtained in the metallic state.

The platinum-solution is filtered off from the insoluble residue, which is collected on a weighed filter and washed. It consists of osm-iridium, and is farther treated as in No. 66.

The solution is much concentrated by evaporation, mixed with a warm saturated solution of sal-ammoniac and then with about twice its bulk of alcohol. Platinum and iridium are thus precipitated in the form of ammonio-chlorides. When the platinum preponderates, the precipitate is yellow; when the amount of iridium is large, it is reddish or red. Not being perfectly insoluble in water, the precipitate is washed with alcohol containing chloride of ammonium. When dried it is ignited without being taken out of the filter; to incinerate the filter completely, air should have

access towards the end. By placing a few crystals of oxalic acid in the crucible, the complete reduction is very materially facilitated. Platinum and iridium may then be separated approximatively by very dilute aqua-regia.

This separation is more accurately effected by proceeding

in the following manner.

The concentrated (crude) solution of platinum is mixed with twice its bulk of alcohol, and then with a warm saturated solution of chloride of potassium until no farther precipitate is formed. This consists of the potassio-chlorides of platinum and iridium with traces of rhodium and palladium, and is yellow or reddish, according to the amount of iridium which it contains. It is filtered off and washed with alcohol containing chloride of potassium.

a. When dried, this precipitate is put into a porcelain crucible, and very intimately mixed with an equal weight of carbonate of soda. The filter is incinerated, and its ash added to the contents of the crucible. The mass is then gently heated until it has become black throughout. By this process the platinum becomes reduced whilst the iridium and osmium are oxidized. The mass is then exhausted with water, the alkali extracted by means of hydrochloric acid, the entire mass washed, dried and ignited, the filter being incinerated separately and weighed.

In order to extract the rhodium, the ignited mass is mixed with 6 times its weight of bisulphate of potassa, and fused at a moderate, but long-continued heat. The rhodium-salt formed is extracted with water; the amount of the oxide of rhodium may then be estimated from the loss, or it is precipitated as stated above in the case of the platinum-residue. When reduced with hydrogen it is treated with nitric acid, in order to extract any of the palladium which it may contain.

The mixture of platinum and oxide of iridium is digested with very dilute aqua-regia, and thus part of the platinum extracted. The cleared solution is poured off, saturated with ammonia, evaporated to dryness, and carefully ignited, when pure platinum is left behind.

The residue of platinum and oxide of iridium is mixed with chloride of sodium and concentrated nitro-hydrochloric acid, and evaporated to dryness. The platinum-salt is then extracted from the mass by means of water, whilst oxide of iridium remains undissolved. The latter must be washed with solution of chloride of sodium, and towards the end with solution of chloride of ammonium, in order to prevent its passing through the filter. The oxide is ignited with the filter and reduced to the metallic slate in a current of hydrogen.

The solution of platinum filtered off from the oxide of iridium still contains some iridium. It is evaporated, and the saline mass once more ignited with carbonate of soda as above.

b. The alcoholic solution filtered from the precipitate of platinum and iridium, which contains the rhodium, palladium, iron, copper and some iridium,* is evaporated to dryness, the mass digested with strong nitro-hydrochloric acid, chloride of potassium added, and the whole again evaporated to dryness in the water-bath. The chlorides of iron and copper are then washed out with alcohol and separated by means of sulphuretted hydrogen. The double chlorides of rhodium, palladium and iridium, which remain undissolved, are fused with bichromate of potassa, and the mass treated with water, when oxide of iridium remains behind.

^{*} It contains no ruthenium, which appears to be present only in the undissolved osm-iridium.

The solution is neutralized with carbonate of soda, and the palladium precipitated by a solution of cyanide of mercury. The yellowish-white cyanide of palladium having settled, it is filtered off, washed and ignited, when metallic palladium is left behind.

The filtered solution is boiled with hydrochloric acid until it has assumed a red tint, and the hydrated oxide of rhodium is then precipitated by caustic potassa. By ignition in hydrogen it is reduced to the metallic state.

From the solution which contains the rhodium and palladium both metals may also be precipitated by pure zinc, with the addition of hydrochloric acid, the precipitate washed, and the palladium extracted by nitric acid, in which the rhodium is insoluble.

If the rhodium be not reduced by formic acid, the solution obtained with bisulphate of potassa might also be mixed with formate of soda and boiled, when palladium is separated in the metallic state. If both be reduced, the palladium could be extracted from the mixture by means of nitric acid.

66. PLATINUM-RESIDUES.*

(From the solution of the crude platinum-ore in nitrohydrochloric acid, consisting chiefly of scales and grains of osm-iridium, of the powder of iridium, of magnetic-, titanic-, and chromic-iron-ores, and sometimes also of some platinum and gold.)

The coarse granular residue is first pounded and triturated as finely as possible, to reduce the grains of the iron-

^{*} To be obtained from St. Petersburg or Paris.

ores to powder. It is then levigated with water, when most of the osm-iridium is separated in larger grains and scales.

The levigated black powder is intimately mixed with about its own bulk of decrepitated and finely-powdered chloride of sodium, the mixture introduced into a porcelain or glass tube, and gently ignited in a slow current of undried chlorine-gas until the latter commences to pass through the tube unabsorbed.

The other end of the tube dips into a well-cooled, tubulated receiver from the tubulure of which a gas-tube conducts the excess of chlorine into alcohol.

By this process sodio-chlorides of iridium and of osmium are formed. The greater portion of the latter is decomposed by the moisture of the chlorine-gas, and the osmic acid formed from it partly sublimes in the receiver, and is partly conducted into the alcohol.

The residue in the tube, when cold, is treated with water, and is at last washed with hot water.

The dark yellowish-red solution of iridium filtered off from the iron-ore is mixed with concentrated nitric acid and distilled, when osmic acid passes over, dissolved in water. The liquid thus very much concentrated, is, whilst still hot, mixed with a saturated solution of sal-ammoniac, when, on cooling, a great portion of the iridium separates in the form of crystalline dark red ammonio-chloride of iridium, which is filtered off and several times washed with solution of chloride of ammonium. On ignition it leaves grey spongy iridium.

A small amount of platinum in this salt can be detected by dividing it very finely, pouring 8 times its weight of water on it and passing sulphurous acid through the latter, when the iridium-salt is dissolved, whilst the platinum-salt is left behind of a yellow colour. The remaining solution is mixed with crystallized carbonate of soda in excess, evaporated to dryness, the mass gently ignited in a crucible, and when cold, washed with hot water, which usually acquires a yellow colour, owing to the presence of an alkaline chromate.

The black powder which is left undissolved, consists of a compound of sesquioxide of iridium with soda, contaminated with sesquioxide of iron. It is reduced by being gently heated in a current of hydrogen. Water then extracts caustic soda, and the iron is removed by digestion with hydrochloric acid. On digesting it, after this treatment, with some very dilute nitro-hydrochloric acid, a small amount of platinum is usually extracted, which may then be precipitated with chloride of ammonium.

The iridium thus purified is washed, submitted to a very powerful pressure, and exposed in a crucible to as strong a white heat as possible, when it is obtained in a somewhat coherent, dense state.

In order to extract the ruthenium, the iridium, previously to ignition, is to be fused for at least an hour, in a silver crucible, with a mixture of nitrate and hydrate of potassa. The mass is treated with water, the yellow solution of ruthenate of potassa poured off (not filtered), the undissolved oxide of iridium repeatedly washed by decantation, and the solution of ruthenate of potassa neutralized with nitric acid, when black sesquioxide of ruthenium is precipitated. By ignition in hydrogen it is reduced to metal, like the oxide of iridium.

In order to detect any rhodium in the iridium, it is fused at a moderate, out long-continued heat, with bisulphate of potassa, and the rhodium-salt formed is then extracted by water. The solution, which is yellow, is boiled with hydrochloric acid, when it becomes red, chloride of

rhodium being formed. Potassa precipitates from it a brownish-yellow hydrated oxide. By ignition in hydrogen it is reduced. During this treatment with bisulphate of potassa, the iridium is likewise converted into black sesquioxide, but is not dissolved.

For the purpose of reducing the osmium from the osmic acid, the latter, in the state of vapour, is mixed with hydrogen and passed through a glass tube heated to redness at one part; or the solution of osmic acid is mixed with formic acid and heated; or it may be mixed with ammonia and chloride of ammonium, evaporated to dryness, and the mass heated in a retort until all the chloride of ammonium is volatilized, when bluish-black osmium remains behind.

The platinum-residue, when once treated in the above manner, is not yet exhausted; by repeating the same operation, more osmium and iridium may be obtained from it.

When the solution of iridium contains gold, it may be precipitated by heating with oxalic acid.

The pure grains of osm-iridium, which contain also ruthenium, can be treated in the same manner, after they have been powdered as finely as possible in a steel mortar, and again freed from iron by hydrochloric acid. The mass, after being ignited in chlorine-gas, is dissolved in water, a few drops of ammonia added to the solution, and heat applied, when a mixture of the oxides of ruthenium, osmium and iridium is separated. By distilling the precipitate with nitro-hydrochloric acid, the osmium is separated in the form of osmic acid. The residue in the retort is evaporated to dryness, the mass fused at a red heat with a mixture of nitrate and hydrate of potassa, dissolved in water, the yellow solution of ruthenate of potassa poured off from the oxide of iridium, and carefully neutralized with nitric acid, when black oxide of ruthenium is precipitated.

Or the entire grains are fused in a capacious platinum crucible, over a spirit-lamp, with a mixture of equal parts of hydrate and chlorate of potassa; from the cold mass water extracts osmate and ruthenate of potassa, and black oxide of iridium is left behind, mixed with unoxidized grains. The solution must not be filtered.

67. PALLADIUM.

The palladium of commerce, usually contains iron and copper, and sometimes also silver. In order to prepare the pure metal from it, it is dissolved by the aid of heat in dilute nitro-hydrochloric acid; the solution is then diluted and the chloride of silver filtered off. The filtrate is then concentrated to a great extent by evaporation, and mixed with ammonia in excess, when, in addition to the sesquioxide of iron, dark flesh-coloured ammoniochloride of palladium is precipitated. When digested with ammonia for a longer period, the latter is dissolved, leaving the sesquioxide of iron, which is separated by filtration. The solution is then mixed with strong hydrochloric acid in slight excess, when most of the palladium is precipitated in the form of lemon-coloured, crystalline chloride of palladamine (NPdH₃ Cl). The precipitate is filtered off after the lapse of twenty-four hours, and washed with as cold water as possible, but only until the washings are free from copper. When dried it is very gradually heated to ignition. It then leaves 50 per cent of bluish spongy palladium.

The solution containing the copper still retains some palladium; it is mixed with an alkaline formate and heated to boiling, when the remainder of the palladium is precipitated in the metallic state. In this manner, at least when operating with small quantities, all the palladium may be precipitated from the original solution; it is then, however, not quite free from copper.

Another method of purifying palladium consists in mixing the nitro-hydrochloric solution of the crude palladium with a quantity of chloride of potassium, amounting to 1½ times that of the metal employed; the solution is then evaporated to dryness, taking care to add towards the end a little nitro-hydrochloric acid. By this process, dark red, crystalline potassio-chloride of palladium is formed; this is to be finely divided, mixed with alcohol, filtered, and washed with alcohol, which dissolves all the chlorides of iron and copper. The salt is then exposed in a porcelain crucible to a strong white heat, either by itself, or mixed with some sal-ammoniac or oxalic acid, and the chloride of potassium extracted with water.—Palladium can readily be fused on charcoal by means of the oxygen blow-pipe.

68. TELLURIUM-ORE.*

The powdered ore contains graphic and foliated tellurium-ore; *i. e.*, the tellurides of gold, silver, lead, and sulphide of tellurium, mixed with various other minerals.

In order to remove a great portion of the gangue, the finely-powdered ore is mixed with dilute hydrochloric acid, with which it is left in contact until no farther disengagement of carbonic acid takes place, the whole being frequently agitated by stirring. It is then washed and

^{*} The telluriferous gold-ores of Transylvania may be obtained in the powdered state, through the kindness of Professor Schrötter, at Vienna, for the value of the gold they contain.

dried. Various methods can be used to extract the tellurium and to recover at the same time the noble metals.

I. The ore is dissolved in nitro-hydrochloric acid, with the precaution, however, that the nitric acid is only gradually added, and in such quantities that it may all be decomposed. When the mass has become completely white and all the nitric acid has been expelled by heat, some sulphuric and tartaric acids are added, the former to ensure the complete precipitation of the lead and the decomposition of the tellurite of lead, the latter to prevent the precipitation of tellurous acid; after this, about twice its bulk of water is added to the mass. When completely cold, the solution is filtered off and the residue washed. The latter consists of quartz, heavy spar, sulphate of lead, and a small quantity of chloride of silver, which may be extracted by ammonia.

From the solution the gold is precipitated by a concentrated solution of sulphate of protoxide of iron. When the metal has subsided, it is washed and ignited.

The liquor filtered off from it is considerably concentrated by evaporation in a flask, allowed to cool, and mixed with a solution of an alkaline sulphite, when the tellurium is precipitated as a grey powder. After standing for twelve or twenty-four hours it is filtered off, and washed, first with dilute sulphurous acid, and then with water.

Gold and tellurium may also be precipitated together by an alkaline sulphite, and the latter metal then extracted by means of nitric acid. The filtered liquid is again evaporated to a small bulk, and mixed with an alkaline sulphite, when, in most cases, a farther quantity of tellurium is obtained. II. The ore, freed from most of the gangue by means of hydrochloric acid, is intimately mixed with twice its weight of bisulphate of potassa; 4 to 6 times its quantity of bisulphate of potassa is then fused in a capacious Hessian crucible at a gentle heat, and into the fusing salt the abovementioned mixture is introduced by small portions at a time, waiting between each addition, until the frothing of the mass has subsided. When this has ceased, and a sample of the mass being taken out appears quite white, the fused mass is poured off from the gold, which has settled at the bottom of the crucible. The remainder of the salt is then washed out of the crucible with hot water containing sulphuric acid, and the gold collected.

The mass which was poured off is then dissolved in this water, with a farther addition of sulphuric acid, the solution filtered off from the sulphate of lead, &c., and then the silver precipitated by means of hydrochloric acid.

The filtered solution is concentrated by evaporation, and the tellurium precipitated by sulphurous acid.

The tellurium thus obtained is not quite pure. In order to purify it, it is distilled in a tube of hard glass, at a strong red heat, in a current of hydrogen. The traces of lead and copper remain behind as tellurides, and a slight admixture of selenium is carried off by the gas.

Accurate quantitative analyses of pure graphic tellurium and foliated tellurium are best made by means of chlorine gas, as in the case of fahl-ores. Tellurium is volatilized in this process as chloride of tellurium; it requires, however, a very wide tube, on account of its being very bulky.

From the telluride of bismuth (tetradymite) of Schemnitz, in Hungary, the tellurium is best obtained by the following process: The finely-divided ore is intimately mixed with 3 times its weight of ignited cream of tartar, and exposed

to a moderate red heat in a covered crucible during one hour, when all the tellurium is converted into telluride of potassium, and the bismuth separated. The cold mass is reduced to powder, thrown on a filter, and completely washed with cold water which has been freed from air by boiling. The dark-red solution of telluride of potassium passing through the filter, when exposed to the air, soon deposits all the tellurium in the form of a grey powder. This method is not applicable to graphic and foliated tellurium-ore.

69. MESOTYPE.*

(NaO, $SiO_3 + Al_2O_3$, SiO_3) + 2 HO.

The amount of water is determined by igniting a weighed quantity of the material, which has previously been dried at 100°.

The finely-divided, unignited mineral, dried at 100°, is mixed in a porcelain dish with moderately strong hydrochloric acid, and digested with it, with constant stirring, until the mass is completely converted into a jelly, and all the mineral is dissolved.

This mass is then evaporated to complete dryness, being carefully stirred, in order to render the silica insoluble; the evaporation is best effected, at least towards the end, in the water-bath.

The remaining salt mass is moistened with hydrochloric acid, after some time a little hot water is poured upon it,

* The yellow variety, the so-called Natrolite, from the phonolite of Hohentwiel, in the Högau, Würtemburg, is most easily procured.

and the silica filtered off, washed with hot water, dried, carefully ignited and weighed.

From the filtered solution the alumina is precipitated by sulphide of ammonium, and treated as in No. 15.

When the zeolite contains sesquioxide of iron, the alumina is coloured more or less black or greenish-black by sulphide of iron. The iron is separated from it as in No. 19.

The solution filtered from the alumina is evaporated to a small bulk, in a dish, transferred to a weighed platinum crucible, and carefully evaporated to dryness. The saline mass is gradually heated till the sal-ammoniac is volatilized, and finally heated to redness, the cover being loosely placed upon the mouth of the crucible. The residue is chloride of sodium.

The silicic acid obtained in the decomposition of a silicate, especially if it separate rather in a pulverulent than a gelatinous state, must always be examined as to its purity, since it may sometimes contain other constituents of the mineral, especially alumina, or even portions of the undecomposed mineral itself.

Pure silicic acid must entirely dissolve in a boiling solution of carbonate of soda. An insoluble residue indicates an impurity, which should be filtered off and examined. It is preferable, however, to fuse such silicic acid with 3 parts of carbonate of potassa and soda, and to treat it as in No. 74.

Silicic acid, if perfectly pure, when dissolved in hydrofluoric acid, in a platinum capsule, entirely disappears on evaporation. Should there be any residue, it is again treated with hydrofluoric acid, afterwards with concentrated sulphuric acid, evaporated to dryness, and examined. It sometimes consists of, or contains titanic acid.

70. LIEVRITE.*

3 CaO, $SiO_3 + 2$ (3 FeO, SiO_3) + 2 Fe₂O₃, SiO_3 .

The finely-powdered mineral is moistened with a suitable quantity of water, in a porcelain capsule, some concentrated hydrochloric acid and a little nitric acid added, and the whole heated to complete gelatinization. The mass is then evaporated to perfect dryness on a water-bath, during which operation it is frequently stirred.

The dry mass is moistened with concentrated hydrochloric acid, then dissolved in chlorine-water, the silicic acid filtered off, and treated in the usual manner (No. 69).

From the solution, diluted with the washing-water, the sesquioxide of iron is precipitated by ammonia, the precipitate allowed to subside in a covered vessel, and rapidly filtered off; the solution should first be passed through the filter, which is kept covered, as far as possible, to prevent absorption of carbonic acid. The precipitate is washed by means of the wash-bottle arranged for the purpose, dried, ignited, and weighed as sesquioxide of iron.

The filtrate from the sesquioxide of iron is acidulated with hydrochloric acid, concentrated by evaporation, in a flask, mixed with ammonia, the lime precipitated by oxalate of ammonia, and treated as in No. 12.

The mineral contains about 1.5 per cent of protoxide of manganese, and 0.5 per cent of alumina, both which are

^{*} The compact variety from Elba is not rare. It may also be obtained artificially by fusing together 6 parts of smithy-scales, 3 parts of fine white quartz-sand, and $1\frac{1}{2}$ parts of calcined marble, at a strong white heat.

contained in the precipitated sesquioxide of iron, and must be separated from it as in Nos. 23 and 19.

About 1.5 per cent of water is also present as an unessential constituent; its quantity may be ascertained by ignition in a covered crucible.

In order to ascertain directly the relative amounts of protoxide and sesquioxide of iron, the process described in No. 22 must be followed.

71. OLIVINE.

3 (FeO, MgO), SiO₃.

The very finely-powdered mineral is decomposed by digestion with concentrated hydrochloric acid, the mass dried upon the water-bath, moistened with concentrated hydrochloric acid, and, after some time, mixed with water and filtered from the separated silica.

Small amounts of copper and tin, which are contained in many specimens of olivine, are detected and separated by mixing the solution with saturated sulphuretted hydrogen-water, until it smells strongly, and allowing it to stand for some time in a closed vessel.

The solution filtered from the precipitate is concentrated by evaporation, some chlorate of potassa being added to peroxidize the iron.

By mixing the cooled solution with chloride of ammonium and ammonia, the sesquioxide of iron may be precipitated and separated from the magnesia. A small quantity of the latter, however, is always precipitated with the sesquioxide.

A better method consists in treating the solution with a

slight excess of carbonate of baryta, and allowing it to digest for twelve hours, with frequent agitation; the precipitate is then filtered off, and treated as in No. 23, III; the small amount of alumina which it contains may also be separated (No. 74).

The baryta must be precipitated from the solution by dilute sulphuric acid, and the filtrate neutralized with ammonia.

This filtrate contains, besides magnesia, a small quantity of protoxide of manganese and protoxide of nickel, which latter is wanting only in the olivine of meteoric iron. These are precipitated by sulphide of ammonium, an excess of which is, as far as possible, to be avoided. The precipitate is not to be filtered off until it has separated so as to leave the solution perfectly clear; it may then be washed with very dilute sulphide of ammonium. If both metals are present only in small quantities, the sulphide of manganese may then be separated from the sulphide of nickel by treating it, upon the filter, with very dilute hydrochloric acid, in which the sulphide of nickel is, practically, insoluble. The small quantity of sulphide of nickel is then ignited in air, and weighed as protoxide. The manganese is precipitated from the solution by carbonate of soda, at a boiling heat.

The liquid filtered from the precipitate produced by sulphide of ammonium, is mixed with ammonia, and the magnesia precipitated by phosphate of soda (No. 6).

In the analysis of olivine, the iron, when converted into sesquioxide, may also be separated from the other bases by succinate of ammonia (No. 23).

72. DATOLITE.

$3 (CaO, BO_3) + 3 CaO, 3 HO, 4 SiO_3.$

For the determination of water, a weighed quantity of the mineral is heated to bright redness.

If the unignited mineral, in a finely-powdered state, be digested with moderately strong hydrochloric acid, it becomes a gelatinous mass. If the mixture be heated to boiling, and filtered while hot, boracic acid separates from the solution in crystals.

No accurate method is at present known for the direct estimation of boracic acid; its amount must, therefore, be inferred from the loss.

The finely-powdered mineral is decomposed by digestion with hydrochloric acid, and the mass evaporated to dryness, when a great part of the boracic acid is volatilized; after exposure for a considerable time to a temperature of 100°, the residue is heated with water containing hydrochloric acid, the silicic acid filtered off, washed, dried and ignited.

The filtrate is neutralized with ammonia, and the lime precipitated by oxalate of ammonia (No. 12).

73. FELDSPAR.

KO, $SiO_3 + Al_2O_3$, $3SiO_3$.

I. The very finely-powdered and levigated mineral, dried at about 200°, is very intimately mixed, in a capacious platinum crucible, with 4 or 5 parts of carbonate of baryta; the crucible is then enclosed in an earthen crucible, which is placed in a wind-furnace with a good draught, and exposed for at least half-an-hour to an intense white heat,

so that the contents may be firmly aggregated into a cinder-like mass. The decomposition takes place more rapidly, and with greater certainty, when the crucible is exposed to a blow-pipe flame, so that the mass fuses completely.

Or the mineral is mixed, in a silver crucible, with 4 parts of hydrate of baryta, previously freed by heat from its water of crystallization, and the mixture heated to fusion.

The mass is then turned out of the crucible into a capacious dish, a quantity of water poured over it, and hydrochloric acid gradually added in slight excess, until, with the aid of a gentle digestion, it is completely decomposed and dissolved, with exception of some gelatinous silicic acid which is separated. The whole solution is then evaporated to perfect dryness, in order to render the silicic acid insoluble, the evaporation being conducted towards the last upon a water-bath, with constant stirring.

The saline mass is afterwards moistened with hydrochloric acid, a proper proportion of water added, and, after digestion, the silica filtered off, washed, thoroughly dried, ignited, and weighed in a covered crucible.

From the solution the baryta is precipitated by gradual and cautious addition of dilute sulphuric acid, a great excess of which is to be carefully avoided; the sulphate of baryta is then filtered off and washed. (See No. 3.)

The filtrate is concentrated, if need be, by evaporation, the alumina precipitated by sulphide of ammonium, and treated as in No. 15.

The liquid filtered from the alumina is evaporated to dryness, and the dry mass ignited to expel the ammoniacal salts. This process requires so much the more care, to avoid spirting, the more sulphate of ammonia it contains, in consequence of the careless addition of sulphuric acid.

At the end of the operation, in order to convert any alkaline bisulphate into neutral sulphate, a fragment of carbonate of ammonia is held in the covered crucible.

The residue is sulphate of potassa, and is weighed as such. Should soda also be present in the mineral, the residue must be treated as in No. 4.

Another method consists in precipitating most of the baryta from the original solution by gradually and cautiously adding dilute sulphuric acid; the rest of the baryta, together with the alumina, is then precipitated by a mixture of carbonate of ammonia and free ammonia, added in slight excess.

After twenty-four hours, the precipitate is filtered off, washed, the alumina (together with the baryta) extracted by dilute hydrochloric acid, precipitated by freshly-prepared sulphide of ammonium, and rapidly washed, with as little exposure to air as possible.

The liquid containing the alkali, filtered off from the precipitate produced by carbonate of ammonia, is concentrated by evaporation, acidified with hydrochloric acid, evaporated to dryness, and the saline mass heated in a covered crucible ultimately to redness; the residue is chloride of potassium (or chloride of sodium). It must be tested for baryta with sulphuric acid, since carbonate of baryta is not absolutely insoluble, and would have been converted into chloride of barium by ignition with salammoniac.

II. A second method of decomposing feldspar is that with hydrofluoric acid. The levigated mineral is placed in a platinum dish, or in a capacious platinum crucible, mixed with a suitable quantity of fuming hydrofluoric acid, and digested with it to complete decomposition.

Or the mineral may be spread out in a shallow platinum

capsule, moistened with water, and exposed for a long time to the vapour of hydrofluoric acid, in an appropriate leaden vessel closed with a lid. The hydrofluoric acid is evolved from powdered fluor-spar, which is placed at the bottom of the vessel, moistened with concentrated sulphuric acid, and gently heated.

When the decomposition of the feldspar is completed, the mass is gradually and cautiously mixed with pure concentrated sulphuric acid, and evaporated, slowly and carefully, to dryness. All the fluorine and silicon are thus expelled, and after the volatilization of the excess of sulphuric acid, the bases remain as sulphates.

The dry mass is moistened with concentrated sulphuric acid, and after a little time mixed with water, in which, if the decomposition be complete, it should entirely dissolve.

From this solution the alumina and alkalies are separated as directed above.

A small quantity of iron, which is frequently present, is to be sought in the alumina.

In the analysis of a feldspar containing lime (labradorite, anorthite), the latter is precipitated, after the separation of the alumina, by oxalate of ammonia.

When petalite and spodumene are analyzed by the above methods, a mixture of salts of soda and lithia is obtained at last, and must be analyzed as in the case of triphylline.

74. AUGITE, HORNBLENDE, GARNET, IDOCRASE, EPIDOTE.

Silicates of CaO, MgO, FeO, MnO and Al₂O₃.

The very finely-powdered mineral must be decomposed by fusion with 4 parts of carbonate of potassa and soda.

The mass is softened with water, dissolved in hydrochloric acid, the silica rendered insoluble by evaporation, as in the analysis of feldspar; the dry mass moistened with hydrochloric acid, dissolved in chlorine-water, in order to oxidize the iron and manganese, and the silicic acid filtered off.

From the solution, the alumina, sesquioxide of iron and sesquioxide of manganese, are precipitated by ammonia.

The lime and magnesia are precipitated from the filtrate, and separated, as in No. 12.

The precipitate, which, besides alumina, sesquioxide of iron and sesquioxide of manganese, may also contain magnesia, is dissolved in hydrochloric acid, the solution heated to boiling, in order to convert the sesquichloride of manganese into protochloride, diluted with much water, and gradually neutralized, with constant stirring, by carbonate of soda; so that the solution may be saturated with carbonic acid, and the addition of the last portions of carbonate of soda may give rise to the formation of bicarbonate.

In this manner the sesquioxide of iron and alumina are entirely precipitated, while magnesia and protoxide of manganese remain in solution.

The two former are then filtered off, and separated as in No. 19.

The solution filtered from the iron- and alumina-preci-

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pitate is mixed with more or less hypochlorite of soda, according to the quantity of manganese present, and allowed to stand for twenty-four hours, when the manganese is entirely precipitated as hydrated sesquioxide, which is converted by ignition into proto-sesquioxide.

The filtrate is concentrated by evaporation in a flask placed obliquely, acidified with hydrochloric acid, taking care to avoid loss by spirting, mixed with ammonia in excess, and the magnesia precipitated by phosphate of soda, as in No. 6.

When a mineral of this description contains very little lime or protoxide of manganese, the solution filtered from the silica may be precipitated at once with bicarbonate of soda, which throws down the alumina and sesquioxide of iron, leaving protoxide of manganese, lime and magnesia in solution.

The alumina and sesquioxide of iron may also be precipitated from the solution by carbonate of baryta, and farther treated as in No. 23.

These and all similar minerals, not attacked by hydrochloric acid, may likewise be conveniently decomposed by hydrofluoric acid; in which case, however, the silica must be determined by loss. (See Feldspar.)

75. BERYL.*

Be_2O_3 , $2SiO_3 + Al_2O_3$, $2SiO_3$.

The very finely-powdered mineral, previously well dried, is fused in a platinum crucible with 4 times its weight of

* The beryl from Haddam in North America, from Limoges in France, from the Rabenstein near Zwiesel, Bavaria, may be easily procured.

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carbonate of potassa and soda (see No. 10); the mass is softened with water, digested with excess of hydrochloric acid until the decomposition is complete, and evaporated to perfect dryness to render the silica insoluble. residue is moistened with hydrochloric acid, and treated with warm water; the silica is then filtered off, the solution concentrated by evaporation, and dropped very gradually, with constant stirring, into an excess of a warm concentrated solution of carbonate of ammonia, which precipitates the alumina, and dissolves the berylla (glucina). When the precipitate has been digested for some time with the solution in a closed vessel, the solution is filtered off, boiled for a long time, until the greater part of the carbonate of ammonia is expelled, slightly acidified with hydrochloric acid, digested for some time to expel the carbonic acid, and the berylla finally precipitated by caustic ammonia.

If it be intended to obtain merely the berylla, it is only necessary to boil the ammoniacal solution, when, in proportion as the carbonate of ammonia is volatilized, the berylla separates as carbonate.

The following is another method: The two earths are precipitated by ammonia, the precipitate filtered off, the greater part detached from the filter, and the remainder dissolved off it in a cold solution of potassa, the filter being afterwards well washed. The alkaline solution is allowed to flow upon that portion of the precipitate which was separated, and potassa is afterwards added until the precipitate is completely dissolved. Any sesquioxide of iron which remains must be filtered off.

The solution is then diluted with much water, and boiled for fifteen minutes, when all the berylla is precipitated. It must be filtered while hot, and the precipitate washed with hot water. The alkaline solution of alumina is feebly acidified with hydrochloric acid, and the alumina precipitated by sulphide of ammonium.

A third method consists in boiling the hydrated earths, freshly precipitated by ammonia, with a concentrated solution of chloride of ammonium, as long as ammonia is evolved, when the berylla passes into solution, and the alumina is left.

76. TOPAZ.*

$6 (3 \text{ Al}_2\text{O}_3, 2 \text{ SiO}_3) + (3 \text{ Al}_2\text{F}_3 + 2 \text{ SiF}_3).$

At a very intense white heat, the topaz loses all its fluorine in the form of terfluoride of silicon.

When fused, in the state of very fine powder, with 4 times its weight of anhydrous carbonate of soda, it is decomposed, with formation of fluoride of sodium, which is extracted by water. Before filtering off the residual silicate of alumina, however, the solution should be digested with some carbonate of ammonia, in order to precipitate any small quantities of alumina and silica which may have been dissolved.

The residue is then filtered off, washed with dilute carbonate of ammonia, and farther treated as in No. 69.

The alkaline filtrate is concentrated and freed from ammonia by evaporation, and the greater part of the carbonate of soda neutralized by nitric acid, so that some carbonate may still remain undecomposed. The solution is then mixed with chloride of calcium, which precipitates a

^{*} Defective crystals of Brazilian topaz may frequently be obtained at a cheap rate.

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mixture of carbonate of lime and fluoride of calcium. When the precipitate has separated, by the aid of a gentle heat, it is filtered off, washed and ignited. The carbonate of lime is then dissolved in dilute acetic acid, the solution evaporated to dryness on a water-bath to expel the excess of acid, and the acetate of lime extracted from the dry mass with hot water. The residual fluoride of calcium is filtered off, washed, dried, ignited and weighed. If the precipitate of carbonate of lime and fluoride of calcium had not been ignited previously to the treatment with acetic acid, the fluoride would have entered the pores of the filter, and the filtrate would have been turbid.

77. ZIRCON.

Zr₂O₃, SiO₃.

A carefully-selected specimen of zircon which has been ignited, and thus deprived of colour, is levigated to a very fine powder, and fused, at a good heat, in a platinum crucible, with 4 parts of anhydrous carbonate of soda. The mass is digested with water, which dissolves the silicate of soda, and leaves a silicate of soda and zirconia as a crystalline powder; this is washed and decomposed by digestion with concentrated hydrochloric acid. The mass is dried up in a water-bath, treated with water containing hydrochloric acid, the silica filtered off, and the zirconia precipitated by ammonia.

Another process for decomposing zircon consists in igniting the very finely-levigated mineral with several parts of pure sugar, introducing the mass, while hot, into a tube of very hard glass, in which it is heated to full redness, while a stream of dry chlorine-gas is passed over it. The

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terchloride of silicon which is formed passes off as gas, while the chloride of zirconium sublimes into the cooler portion of the tube.

If the zirconia obtained by the first process contain any iron, the precipitate is digested with oxalic acid, which dissolves the sesquioxide of iron, leaving oxalate of zirconia, at least in part, undissolved.

Or the precipitate may be treated with sulphide of ammonium, to convert the iron into sulphide, the solution once more decanted, and the black precipitate treated with solution of sulphurous acid, which immediately dissolves the sulphide of iron, leaving the zirconia colourless. A shorter method is to heat the solution containing zirconia and iron, after neutralization, with bisulphite of soda, when all the zirconia is precipitated free from iron.

For accurate quantitative separation, the solution of zirconia containing iron is mixed with tartaric acid and excess of ammonia, which should not cause any precipitate; the iron is then removed by sulphide of ammonium, the precipitate allowed to separate completely, filtered off without intermission, and washed with dilute sulphide of ammonium. The solution is evaporated to dryness, and the residue ignited, till all the carbon has burnt off, and the zirconia has become white.

From a neutral solution, zirconia is completely precipitated by a boiling saturated solution of sulphate of potassa, as a white pulverulent double salt. After boiling, this precipitate is sparingly soluble in water, and even in acids:

The substance usually termed zirconia is said to consist of several very similar oxides, which have not been accurately separated from each other. 118 CERITE.

78. CERITE.*

3 (CeO, LaO, DiO, FeO, CaO), $SiO_3 + 3$ HO.

Cerite, in fine powder, is treated with concentrated sulphuric acid, with which it is digested, until the high temperature produced by the combination has caused it to form a dry mass.

Cold water is then poured over it, and the mixture allowed to digest, in the cold, until the sulphates are dissolved. The solution filtered from the silica, which must be concentrated by evaporation if too largely diluted by the washings, is mixed with a boiling saturated solution of sulphate of potassa, and allowed to cool. Cerium, lanthanium and didymium are thus precipitated as double sulphates, while iron, &c., 'remain dissolved. The precipitate is filtered off, and washed with a saturated solution of sulphate of potassa. Crystalline crusts of sulphate of potassa are placed in the filtrate, and in this way the remainder of the double salt is precipitated.

The precipitated salt is dissolved in the necessary quantity of boiling water, with addition of some hydrochloric acid, and the bases precipitated from the hot solution by an excess of caustic potassa. (Ammonia precipitates basic salts.)

After ignition, they appear as a cinnamon-brown powder. When converted into sulphates by digestion with concentrated sulphuric acid, they give, with water, a yellow solution, from which sulphate of potassa precipitates a lemon-yellow mixture of double salts.

Another method of obtaining the oxide of cerium consists in precipitating the original sulphuric solution, while

* Only to be found in one locality—the mine of Bastnäs, near Riddarhytta in Westmanland. May be obtained from dealers in minerals, or from Stockholm.

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hot, with an excess of hydrate of potassa, washing the precipitate, and digesting it with an excess of solution of oxalic acid, when the iron and lime are dissolved, and the oxide of cerium, &c., left as white oxalates, which are filtered off and washed. By ignition in air, they are converted into the brown oxides.

CERITE.

There is at present no method of accurately separating these three oxides from each other.

The Hydrated Protoxide of Cerium is colourless, but oxidizes rapidly on exposure to air, and becomes yellow.

The Sesquioxide of Cerium, in the pure state, is yellow, with a tinge of red; when impure, it is brick-red. It is produced when the hydrate is ignited in air. The sesquioxide is soluble only in hot concentrated sulphuric acid; the solution has a fine yellow colour. The hydrated sesquioxide is dissolved, in quantity, with a yellow colour, by the alkaline bicarbonates, especially by bicarbonate of ammonia. The sesquioxide is insoluble in concentrated hydrochloric acid, but on addition of alcohol, it is dissolved in the form of protochloride.

OXIDE OF LANTHANIUM is colourless; when heated with water, it is converted into the hydrate, which has an alkaline reaction. It is dissolved by a hot solution of chloride of ammonium, with evolution of ammonia. Its salts are colourless. The carbonate is insoluble in carbonate of ammonia.

OXIDE OF DIDYMIUM, when ignited, is brown. When exposed to a white heat it assumes a dingy white colour, with a tinge of green. It is soluble in acids; its salts have the colour of amethyst, with a tinge of blue; with hydrate of potassa they yield a violet hydrate. The carbonate is insoluble in carbonate of ammonia.

The ignited brown mixture of the three oxides is dissolved by hydrochloric acid, with evolution of chlorine.

If the mixed hydrates, precipitated by potassa, be dissolved in nitric acid, the solution evaporated to dryness, and ignited, a dark brown oxide is obtained, from which a part, at least, of the oxide of lanthanium may be obtained in a pure state. For this purpose, the finely-powdered oxide is mixed with water, to which nitric acid, free from nitrous acid, is added in single drops with continual agitation, in proportion as it is saturated. From the filtered solution, at a boiling-heat, carbonate of ammonia precipitates carbonate of oxide of lanthanium in shining, crystalline scales.

When the oxides precipitated by potassa are mixed with a concentrated solution of potassa, and the latter saturated with chlorine-gas, and frequently agitated, the cerium is converted into an insoluble yellow compound of the sesquioxide, while didymium and lanthanium, together with some cerium, are dissolved as protochlorides. The yellow sesquioxide of cerium is digested still longer with chlorine-water, filtered off, washed, and digested with dilute potassa to remove hypochlorous acid; any potassa which it has taken up is then extracted by dilute nitric acid. The solution of the protochlorides (of didymium and lanthanium) is again precipitated by potassa, and the precipitate treated a second time with potassa and chlorine-gas.

79. ORTHITE.*

YO, CeO, LaO, CaO, MgO, MnO, FeO, Fe₂O₃, Al₂O₃, SiO₃.

The finely-powdered mineral, dried at 100°, is decomposed by digestion, in a porcelain dish, with concentrated

^{*} This is the least rare of the minerals containing yttria. The preparation of yttria from gadolinite, which is much rarer, but contains more of that base, may be effected in a similar manner.

hydrochloric acid, to which some nitric acid has been added, to peroxidize the iron; the mass is completely dried up, with frequent stirring, in a water-bath, and maintained for some time at that temperature.

It is then digested with a little water acidulated with hydrochloric acid, the silica filtered off, washed with hot water, thoroughly dried, ignited and weighed.

The washing-water is evaporated to a small bulk, mixed with the filtrate, and saturated with chlorine-gas to convert manganese into sesquichloride; the solution is precipitated by ammonia, which separates all the bases except lime.

The precipitate is allowed to subside in a closely-covered vessel, the clear liquid rapidly poured through the filter, upon which the precipitate is afterwards thrown (always keeping it covered), and washed thoroughly with hot water by means of the wash-bottle properly arranged for that purpose.

The washings, slightly acidified with hydrochloric acid, are evaporated to a small bulk, mixed with the first filtrate, neutralized with ammonia, and the lime precipitated by oxalate of ammonia. (See No. 12.)

The filtrate, after concentration, is tested for magnesia, since perhaps this base may not have been entirely precipitated with the alumina.

The precipitate produced by ammonia is carefully detached from the filter, while yet moist, without perforating the paper; that portion which cannot be mechanically removed is then dissolved off with a few drops of hydrochloric acid, the filter well washed, the solution added to the other portion of the precipitate, and the latter dissolved in the smallest possible quantity of hydrochloric acid; the solution is afterwards heated for some time nearly to boil-

ing, to convert all the manganese and cerium into protochlorides. When the liquid has become perfectly cool, an excess of finely-powdered carbonate of baryta is added, and the whole allowed to stand for twenty-four hours, with frequent agitation. In this way, all the sesquioxide of iron and alumina are precipitated.

The mixture is filtered, the precipitate well washed, dissolved in hydrochloric acid, the baryta precipitated by dilute sulphuric acid, and the sesquioxide of iron and alumina separated from the filtrate as in No. 19.

In the solution filtered from the precipitate of alumina and sesquioxide of iron, the dissolved baryta is precipitated by dilute sulphuric acid, the precipitate filtered off, and the solution evaporated to a small bulk. It is then mixed with several times its volume of a boiling saturated solution of sulphate of potassa, which precipitates the oxides of cerium, &c. (CeO, LaO, DiO) in the form of a white, pulverulent double salt. After the lapse of twenty-four hours, this is filtered off, and thoroughly washed with a saturated solution of sulphate of potassa, in which it is perfectly insoluble.

It is then dissolved in a sufficient quantity of boiling water, with addition of some hydrochloric acid, the solution precipitated, while hot, by an excess of caustic potassa, the precipitate filtered off, washed, ignited and weighed as brown sesquioxide of cerium. (See No. 78.)

(If a similar mineral contained also zirconia or thoria, these would be present in the precipitate produced by sulphate of potassa, although a part of the zirconia might be found in the precipitate produced by carbonate of baryta. It is insoluble in caustic potassa.)

The solution filtered from the precipitate produced by sulphate of potassa, which still contains the yttria, is neutralized with ammmonia, and the yttria precipitated by oxalic acid. After twenty-four hours, the precipitate is filtered off, washed, ignited and weighed as yttria (YO, TbO, EO).

A little manganese may still be contained in the filtrate. After neutralization, it may be precipitated by pentasul-

phide of potassium.

If the ignited yttria had a brownish colour, it would contain manganese, from which it might be separated by dilute nitric acid, free from nitrous acid; perhaps also the separation might be effected by heating with excess of solution of oxalic acid, since oxalate of yttria is perfectly insoluble in that acid.

(If such a mineral should contain also berylla, it would be found in the solution filtered from the oxalate of yttria, and might be precipitated thence by ammonia.

In order to detect the presence of berylla in yttria, it is necessary, since the latter cannot be extracted by caustic potassa, to mix the precipitate with pure sugar, and to carbonize the mass in a platinum crucible; it is then ignited in a stream of dry chlorine-gas, when the chloride of beryllium sublimes, and chloride of yttrium remains in the carbonized mass.)

The precipitate produced by ammonia, which contains, in addition to lime, all the other bases of the orthite, may also be analyzed by digesting it with an excess of solution of oxalic acid, when the sesquioxide of cerium and the yttria remain undissolved. Before these are separated farther, they must be ignited, to destroy the oxalic acid.

80. THORITE.*

3 ThO, $SiO_3 + 3$ HO.

The finely-powdered mineral gelatinizes entirely with concentrated hydrochloric acid. The solution is evaporated to dryness, the silica filtered off, the filtrate highly concentrated by evaporation, and mixed with a boiling saturated solution of sulphate of potassa. In this way all the thoria, like the oxides of the cerium-class, is precipitated as a white pulverulent double salt. After cooling, this is filtered off, and washed with a saturated solution of sulphate of potassa. It is then dissolved in boiling water and the alumina precipitated by caustic potassa.

After ignition, thoria is white, and has a spec. grav. of 9.4. It can only be dissolved in hot concentrated sulphuric acid. The hydrate of thoria is insoluble in potassa.

Chloride of thorium is fusible, and may be sublimed.

Sulphate of thoria dissolves but slowly in water. When the solution is heated, a tissue of fine crystalline needles separates, consisting of a salt containing less water, which is very sparingly soluble.

81. APATITE.

3 (3 CaO, PO_5) + CaCl (or + CaF).

For the determination of chlorine, a weighed portion of the mineral (which need not be powdered) is dissolved in

* This black, amorphous mineral, from Lövön; near Brevig in Norway, is taken here, without regard to its rarity, as an example of a compound of thoria, in order to direct attention to the detection of this earth, which must certainly occur more frequently. The orange-coloured orangite of Brevig has a similar composition.

dilute nitric acid,* and the chlorine precipitated by nitrate of silver.

In order to detect the small quantity of fluorine which is contained in some specimens of apatite, the finely-powdered mineral is mixed, in a platinum crucible, with concentrated sulphuric acid, and the crucible covered with a glass plate coated with a thin film of wax, through which some characters have been written with a needle; the crucible is then heated with a flame so small as not to melt the wax. If fluorine be present, the characters are found etched upon the glass after the removal of the wax. The quantity of the fluorine is inferred from the loss of weight in the whole analysis.

The phosphoric acid and lime may be determined by the methods described in the analysis of bone-earth. The following process may also be employed.

The mineral is dissolved in nitric acid, in a dish, and so much pure mercury added that, after saturating the acid, a portion still remains undissolved. The mixture is then evaporated to perfect dryness on the water-bath. Should it still emit an odour of nitric acid, this acid must be completely expelled by adding more water, and again evaporating to dryness. The mass is treated with water, filtered through the smallest possible filter, and the residue, which contains all the phosphoric acid, well washed.

The solution contains, besides the excess of the mercurysalt, the whole of the lime. The suboxide of mercury is precipitated by hydrochloric acid. Any protoxide of mercury which may have been formed, is precipitated from the filtrate by ammonia. If the mineral contain iron, or other

^{*} Many compact apatites, when treated with nitric acid, leave a small quantity of a crystalline powder, which is kryptolite (phosphate of protoxide of cerium).

bases precipitable by ammonia, these will remain behind on igniting this precipitate. From the solution, which should be filtered rapidly, and with as little exposure to air as possible, the lime is precipitated by oxalate of ammonia.

The filter with the mercury-residue, which contains the phosphoric acid, is well dried, and the contents thrown into a platinum crucible in which they are mixed with carbonate of potassa and soda; the filter is rolled up and buried in the mixture. The crucible is now heated (but not to redness) under a chimney with a good draught, until the mercury is volatilized, after which the mass may be heated to redness and fused. It is then dissolved in water, an excess of hydrochloric acid added, and the phosphoric acid precipitated by ammonia and sulphate of magnesia.

82. TRIPHYLLINE.*

3 (FeO, MnO, LiO), PO₅.

In order to obtain the lithia, the coarsely-powdered mineral is dissolved in concentrated hydrochloric acid, with gradual addition of nitric acid; the solution is heated, to ensure the conversion of all protoxide of iron into sesquioxide, and poured off from any extraneous minerals which generally remain undissolved. It is then evaporated completely to dryness, being constantly stirred towards the last, and the mass heated until all free acid is evaporated. It is then finely powdered, boiled out with water, and the solution filtered. This now contains not a trace of iron, which

^{*} Occurs in largest quantity in a vein of granite at the Rabenstein, near Zwiesel, in the Bavarian forest. It may also be obtained from Dr. H. Müller, at Weiden in Bavaria.

remains undissolved as white phosphate, but only chloride of lithium, mixed with the chlorides of manganese, magnesium and sodium. In order to precipitate the two former, together with a small quantity of phosphoric acid which may be present, the solution is mixed with pure hydrate of lime, and boiled, with access of air, until all the hydrate of protoxide of manganese is converted into the brown sesquioxide. All the lithia remains in the solution; it is filtered off, and the dissolved lime precipitated by a mixture of carbonate of ammonia and free ammonia. After filtration, the solution is evaporated, and the chloride of lithium heated to fusion in a porcelain crucible.

The chloride of lithium still contains chloride of sodium, which is separated by digesting the mass with a mixture of alcohol and ether, which dissolves the chloride of lithium, and leaves the chloride of sodium undissolved. Or the impure chloride of lithium may be converted into carbonate by dissolving it in the smallest possible quantity of concentrated ammonia, and placing in the solution, which should be kept as cold as possible, fragments of carbonate of ammonia. The precipitated carbonate of lithia is filtered off and washed with alcohol.

Pure chloride of lithium is easily fusible, it imparts to the flame of alcohol a dark carmine-red colour; when soda is present, the colour is rather orange-red.

83. FLUOR-SPAR.

CaF.

A weighed quantity of the finely-powdered mineral is mixed, in a platinum crucible, with concentrated sulphuric acid, and heated until all the hydrofluoric acid is expelled, and the greater excess of sulphuric acid volatilized. The residual sulphate of lime is then mixed with alcohol, filtered off, washed with alcohol, ignited and weighed. Or it may be dissolved in water containing hydrochloric acid, the solution mixed with ammonia, and the lime precipitated by oxalate of ammonia.

The fluorine is determined from the loss. In order to estimate it directly, the decomposition must be effected in a platinum retort, the vapours of hydrofluoric acid conducted into solution of carbonate of soda, and the fluorine precipitated from the solution by chloride of calcium, as in the analysis of topaz.

Or the very finely-powdered mineral may be mixed with an excess—that is, with at least an equal weight—of finelypowdered silicic acid (that prepared from terfluoride of silicon is the best), the mixture introduced into an apparatus similar to that employed in alkalimetry, and the sulphuric acid, which must for this purpose be most concentrated, allowed to flow upon it. With the aid of a gentle heat, terfluoride of silicon is formed, which is allowed to escape in the gaseous state through a tube filled with chloride of calcium; the last portions are withdrawn from the apparatus by sucking air through it, for which purpose, there is attached to the chloride-of-calcium-tube a small tube filled with fragments of moist hydrate of potassa, through which the air is drawn. The loss of weight expresses the amount of terfluoride of silicon which has been evolved, and of which 100 parts correspond to 72.79 of fluorine.

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84. SPHENE (TITANITE).2 (CaO, SiO₃) + CaO, 3 TiO₂.

This mineral, even in the state of very fine powder, is only attacked with difficulty, and at best incompletely, by hydrochloric or sulphuric acid.

It is better to heat it in a platinum capsule with bisulphate of ammonia, gradually raising the temperature, with constant stirring, till the salt fuses; the heat is finally increased to ignition. A little dilute sulphuric acid is then added, and heat again applied until the acid begins to volatilize. When the mass is perfectly cold, it is mixed with water, the silicic acid filtered off, and the sulphate of lime thoroughly washed.

From the solution, the titanic acid is precipitated in the cold, together with the small quantity of sesquioxide of iron, by ammonia, the solution filtered rapidly, with as little exposure to air as possible, and the lime precipitated by oxalate of ammonia.

The titanic acid containing iron is dissolved in hydrochloric acid, the solution mixed with pure tartaric acid and excess of ammonia, which ought not to cause any precipitate. Sulphide of ammonium is afterwards added, to precipitate the whole of the iron. (See Zircon.)

The solution filtered from the sulphide of iron is evaporated to dryness, the mass carbonized, and heated with access of air, or in a stream of oxygen, until all the carbon is burnt off, and the titanic acid is perfectly white.

Another method (in which, however, the silicic acid is determined by loss) consists in decomposing the mineral by concentrated hydrofluoric acid. The mass is afterwards mixed with concentrated sulphuric acid, heated until all the terfluoride of silicon and most of the sulphuric acid are expelled, mixed once more with concentrated sulphuric acid, and heated until it begins to evaporate. The whole may then be dissolved by adding a sufficient quantity of water.

85. TITANIC IRON.* Fe₂O₂, Ti₂O₃, and FeO, Ti₂O₂.

For the analysis of this mineral, and for the preparation of pure titanic acid, various methods are employed. The titanic iron dissolves in concentrated hydrochloric acid, but very slowly. When the levigated powder is ignited in hydrogen-gas, the iron is reduced, and may be extracted by hydrochloric acid; the reduction, however, requires a very long time and an intense red heat, and, after all, the titanic acid is not free from iron. The following methods are more efficient:

1. The very finely-powdered mineral is fused in a platinum crucible, placed within an earthen crucible, with 3 parts of carbonate of potassa; the fused mass is powdered, and dissolved in a platinum capsule, in the requisite quantity of dilute hydrofluoric acid. Titano-fluoride of potassium is thus produced, which is sparingly soluble, and crystallizes readily, while most of the sesquioxide of iron is separated free from titanium. The mixture is heated to boiling, so much water being added as is requisite to dissolve all the salt, and filtered while boiling hot; glass vessels may now be employed, provided an unnecessary excess of hydro-

^{*} Titanic iron occurs in considerable quantity at Egersund in Norway, and may be obtained of the dealers in minerals.

fluoric acid has been avoided. On cooling, the greater part of the salt separates in lustrous crystalline scales. It is filtered off, pressed, washed once or twice with cold water, and purified completely by recrystallization from boiling water.

The sesquioxide of iron is washed, the washing-water mixed with the mother-liquor from the salt, and with the washing-water from the latter, and the dissolved sesquioxide of iron, together with a very little titanic acid, precipitated from the mixed solution, in the cold, by dilute ammonia. The precipitate must be filtered off immediately, for otherwise the titanic acid also begins to separate. The filtrate is then heated to ebullition, when all the titanic acid is precipitated as white titanate of ammonia. In the same manner the titanic acid may be obtained from the crystallized titano-fluoride of potassium previously separated.

The titanate of ammonia is easily soluble in hydrochloric acid, and, at a red heat, is converted, with incandescence, into pure titanic acid.

II. The finely-powdered mineral is fused with at least 6 parts of bisulphate of potassa, in a platinum crucible, until it is completely dissolved; the fused mass, when cool, is powdered and dissolved in cold water.

This solution has the peculiarity, when long boiled, of depositing the whole of the titanic acid, which is not, however, quite free from iron.

In order to obtain it perfectly free from the latter metal, the sesquioxide of iron and titanic acid are precipitated by ammonia, the clear solution decanted from the precipitate, and the latter treated with excess of sulphide of ammonium, which converts all the iron into black sulphide. After standing for several hours, the mixture is diluted with water, the clear liquor decanted, and the precipitate washed once or twice by decantation.

It is afterwards mixed with sulphurous acid, when it immediately becomes white, since the sulphide of iron dissolves in the form of dithionate of protoxide of iron. The titanic acid is filtered off, washed and ignited, a fragment of carbonate of ammonia being held in the crucible to expel any sulphuric acid.

A little more titanic acid separates from the filtrate on standing for some time, and on gently heating. The iron, when converted into sesquichloride by chlorine, or by heating with hydrochloric acid and chlorate of potassa, may be precipitated from the solution by ammonia.

III. Or the whole of the titanic acid, together with the sesquioxide of iron, may be precipitated by ammonia from the solution of the mass obtained by fusion with bisulphate of potassa; the precipitate is washed with cold water, dissolved in hydrochloric acid, the solution treated with sulphurous acid or metallic zinc to reduce the sesquioxide of iron to the state of protoxide, and the titanic acid precipitated by an excess of carbonate of baryta. The precipitate is rapidly filtered off, washed, dissolved in cold hydrochloric acid, the baryta precipitated by sulphuric acid, and afterwards, the titanic acid separated by ammonia.

86. RUTILE.*

TiO2.

In order to obtain pure titanic acid from rutile, the same

^{*} Occurs most abundantly at St. Yrieux, in France, and may be purchased very reasonably.

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method may be employed as for titanic iron; the first process is especially applicable to this purpose.

Another process consists in converting the titanic acid into bichloride. The very finely-powdered rutile is mixed with ignited lamp-black (11 part of carbon for 5 parts of rutile) and so much starch-paste as will suffice to form a plastic mass. This is moulded into cylinders about 1 or 2 inches long, and \(\frac{1}{3}\) of an inch thick, which are slowly dried. They are then thoroughly ignited in a covered crucible, and, while still hot, before they have absorbed any moisture, introduced into a tube of porcelain or of hard glass. A stream of dry chlorine is passed in at one end of the tube, while the other opens into a cooled receiver furnished with an egress-tube. As soon as the apparatus is filled with chlorine, the tube is heated to bright redness, and the separation carried on till no more drops of bichloride of titanium distil over. The carbonic oxide and excess of chlorine are passed into a small quantity of alcohol, which absorbs the latter.

The bichloride of titanium, which has a brown colour due to sesquichloride of iron, is poured into a small tubulated retort containing some mercury or bright copperturnings; the neck of the retort is drawn out to a point, which is bent downwards. When the bichloride of titanium has been left for some time in contact with the metal, it is distilled off by gentle ebullition, and immediately received in tubes, which are afterwards hermetically sealed.

In order to prepare pure titanic acid from the bichloride, it is gradually mixed with water, avoiding all rise of temperature, which would render the solution turbid, and the titanic acid precipitated by ammonia.

Pure ignited titanic acid is white, frequently with a tinge of yellow. During ignition it has a lemon-yellow

colour. When exposed to a very high degree of heat it becomes brownish. It is then perfectly insoluble in hydrochloric acid. By long digestion with concentrated sulphuric acid, it is dissolved.

87. COLUMBITE.

The columbite from Bodenmais in Bavaria, and from Haddam in Connecticut, contains niobic and pelopic acids combined with the protoxides of iron and manganese. The American variety contains the least pelopic acid. Niobic acid is also present, together with titanic acid, in the pyrochlore from Norway and Siberia, in combination with lime, protoxide of cerium and alumina.

The tantalite and yttrotantalite from Finland and Sweden, however, contain tantalic acid, combined, in the former, with the protoxides of iron and manganese, in the latter, with yttria, lime, protoxide of uranium and protoxide of iron.

These minerals, with exception of pyrochlore, which is decomposed by concentrated sulphuric acid, are not attacked by acids.

They are best decomposed by fusing them, in the form of a levigated powder, with 6 parts of bisulphate of potassa, in a platinum crucible. The salt is first fused by itself, allowed to solidify, the powdered mineral thrown upon it, and the two gradually fused together. The fusion is continued until the mineral has entirely dissolved.

The mass is afterwards repeatedly boiled with water, and the undissolved acids filtered off and washed. They still contain sesquioxide of iron, and commonly also small quantities of binoxide of tin and tungstic acid.

The acids are now digested with sulphide of ammonium,

which dissolves the two latter and converts the sesquioxide of iron into sulphide, which imparts a black colour to the acids. This may be effected upon the filter itself, if the stem of the funnel be passed air-tight into a flask; the funnel should be kept as closely covered as possible after the mass upon the filter has been carefully mixed with sulphide of ammonium.

After washing, very dilute hydrochloric acid is allowed to flow over the mass upon the filter, when the sulphide of iron is dissolved, and the acids again become white. They are then washed, dried and ignited, when the sulphuric acid with which they are combined is volatilized, which may be effected with greater rapidity and certainty if a fragment of carbonate of ammonia be held in the closed crucible during the ignition.

Tantalic, pelopic and niobic acids are white powders. They are characterized by the following properties:

Tantalic Acid remains white when ignited. Its hydrate, prepared by decomposing the chloride with water, exhibits, when ignited, a vivid incandescence; it is afterwards insoluble even in sulphuric acid.

The chloride corresponding to tantalic acid is yellowish, volatile, and fusible to a yellow liquid. It fumes in the air without deliquescence; it is partly dissolved by solution of potassa; it is decomposed by water into hydrochloric acid and white hydrated tantalic acid; it is dissolved, but not completely, by hot hydrochloric acid; sulphuric acid produces a white precipitate in the solution.

When strongly ignited in hydrogen-gas, tantalic acid remains white.

Tantalic acid is dissolved in large quantity by phosphorus-salt before the blow-pipe. The bead remains colourless, even in the inner flame.

Pelopic Acid becomes yellow on ignition, and white again on cooling. Its hydrate, prepared from the chloride, exhibits incandescence when ignited; it is afterwards perfectly insoluble in acids.

The chloride of pelopium is yellower than the perchloride of tantalum, which in other respects it entirely resembles. It is partially dissolved by solution of potassa. Its solution in cold hydrochloric acid becomes thick after some time; when diluted with water and boiled, nearly all the pelopic acid is precipitated. If the solution be prepared with the aid of heat, it does not exhibit these properties. This solution is precipitated by sulphuric acid only on boiling.

When intensely ignited in hydrogen, pelopic acid becomes black.

Pelopic acid is dissolved in large quantity by phosphorussalt, before the blow-pipe, to a clear and colourless bead. In the inner flame, the bead becomes brown, with a tinge of violet.

Niobic Acid, precipitated by ammonia, forms, after ignition, compact, very lustrous fragments. During ignition, it has an intense yellow colour, and becomes white again on cooling. The hydrate, prepared from the chloride, exhibits intense incandescence when ignited, and becomes perfectly insoluble in acids; if, however, it have not been too strongly ignited, it is dissolved by warm concentrated sulphuric acid. When diluted with water, the solution, after a long time, allows all the niobic acid to precipitate; this takes place immediately on boiling the solution.

The chloride of niobium is white, very bulky, infusible, and more difficult of volatilization than the chlorides of tantalum and pelopium. It fumes in the air, and is

decomposed by water into hydrochloric acid and a white hydrate. It is not dissolved by hydrochloric acid, nor precipitated by it. When boiled with hydrochloric acid, however, it dissolves, if water be subsequently added; and the solution is not precipitated by boiling, even on addition of sulphuric acid. Chloride of niobium is easily dissolved by solution of potassa.

When strongly ignited in hydrogen, niobic acid becomes

darker than pelopic acid.

Niobic acid is dissolved in large quantity by phosphorussalt, before the blow-pipe, to a clear, colourless bead. In the inner flame, the saturated bead assumes a pure blue colour, without a tinge of violet.

If the chlorides corresponding to these acids are moistened with sulphuric acid, diluted with a little water, and a piece of zinc placed in the mixture, all three acids give a fine blue colour. All the acids, when fused with hydrate of potassa, yield salts which are soluble in water. The soda-salts are insoluble in a solution of soda or carbonate of soda, but dissolve in pure water.

Tantalic acid has not been found at present in company with the other two acids. Niobic and pelopic acids, however, nearly always occur together.

In order to detect one of these acids in the presence of the other, they are converted into the chlorides which are very different in their properties. The acids are mixed with pure sugar and lamp-black, and ignited; the carbonized mass is introduced into a wide tube of very infusible glass, and heated to redness in a current of perfectly dry chlorine.

If the mixed acids contained also titanic acid, the strongly-fuming liquid chloride of titanium would also be formed.

No method is at present known of accurately separating pelopic, niobic and titanic acids. After fusion with bisulphate of potassa, most but not all the titanic acid may be extracted by water. If the sublimate which contains the three chlorides be dissolved in hydrochloric acid, pelopic acid at least (perhaps also niobic acid) may be precipitated by sulphuric acid, while titanic acid remains in solution.

The mixture of acids containing sulphuric acid, which remains after fusion with bisulphate of potassa and treatment with water, is soluble in solution of potassa, as well as in concentrated hydrochloric acid. From the latter solution, pelopic acid (and niobic acid?) may be precipitated by sulphuric acid.

88. WOLFRAM.* (MnO, FeO), WO.

- 1. In order to effect merely a qualitative separation, for obtaining tungstic acid, the very finely-powdered mineral is digested with a mixture of concentrated hydrochloric acid and about \(\frac{1}{4} \) of nitric acid, until it is converted into vellow, pulverulent tungstic acid. This is filtered off, washed, dissolved in ammonia, the solution filtered, and
- * May be obtained very reasonably from Zinnwald or Schlackenwald, in Bohemia, or through the kindness of Dr. Knopp, at Chemnitz.
- + By this treatment, there is left undissolved, besides the undecomposed particles of mineral which have not been finely powdered, a white substance, consisting of silica and niobic acid, of which latter the wolfram contains about 2 per cent. In order to remove the silica, it is repeatedly evaporated with hydrofluoric and sulphuric acids, then fused with bisulphate of potassa and farther treated as directed for columbite.

evaporated to crystallization. On igniting the salt in the air, pure yellow tungstic acid is left.

Or the finely-powdered wolfram is mixed with 4 parts of carbonate of soda, and an equal weight of sulphur, the mass heated till it enters into tranquil fusion (which is best effected in a cast-iron crucible), powdered, boiled with water, and filtered. From the dark red-brown solution, the sulphide of tungsten is precipitated by dilute sulphuric acid, the precipitate washed, dried and ignited, with access of air, in a large crucible placed obliquely, until it is converted into tungstic acid, which is purified by solution in ammonia.

Again, 3 parts of the mineral, very finely powdered, may be mixed with 3 parts of carbonate of potassa, and the mixture heated to redness for half-an-hour the tungstate of potassa which has been formed may be extracted from the cooled mass with water.*

From this solution, the tungstic acid may be separated by two different methods:

- a. The solution is neutralized with nitric acid and mixed with nitrate of suboxide of mercury, as long as any precipitate is produced. The precipitated salt is washed, dried, and heated in a glass retort, when mercury distils over, and pure tungstic acid is left.
- b. The neutralized solution is precipitated by chloride of calcium, the precipitated tungstate of lime washed, and boiled with hydrochloric acid, when pure yellow tungstic acid remains behind.
 - II. For quantitative analysis, the levigated mineral is

^{*} On dissolving the residual proto-sesquioxides of iron and manganese or the metallic sulphides obtained as above mentioned in concentrated hydrochloric acid, niobic acid remains behind.

digested with a mixture of 4 parts of concentrated hydrochloric acid and 1 part of nitric acid, until it is completely decomposed; the solution is then evaporated to dryness, which operation should be finished on the water-bath, the chloride of manganese and sesquichloride of iron dissolved out, the tungstic acid filtered off, washed with alcohol, dissolved in ammonia, separated by filtration from the niobic acid, the solution evaporated, the residual ammonia-salt ignited with access of air, and the tungstic acid weighed.

The filtrate, containing alcohol, is evaporated to expel the latter, diluted with water, and the oxides of manganese and iron separated as in No. 23. They usually contain a little lime.

Or the levigated mineral is ignited, in a platinum crucible, with 3 parts of carbonate of potassa, the mass dissolved in water, the residual oxides thoroughly washed, the solution neutralized with nitric acid, and the tungstic acid precipitated by nitrate of suboxide of mercury, the free nitric acid being afterwards neutralized with a few drops of ammonia, so that a black precipitate begins to appear. The precipitate is thoroughly washed, a very dilute solution of nitrate of suboxide of mercury being used at last, since otherwise, the precipitate is liable to pass through the filter; it is then dried and ignited, when pure tungstic acid is left.

The mixture of the oxides of iron and manganese is dissolved in concentrated hydrochloric acid, which usually leaves undissolved a small quantity of tungstic, niobic and silicic acids. The two oxides are then separated as in No. 23.

89. SCHEELITE. CaO, WO₂.

The minera, very finely powdered, is digested with concentrated nitric acid, the mass evaporated nearly to dryness, mixed with alcohol, and filtered. The residual yellow tungstic acid is washed with alcohol, ignited and weighed. The alcohol is expelled from the solution by evaporation, the latter neutralized with ammonia, and the lime precipitated by oxalate of ammonia.

90. MOLYBDATE OF LEAD.* PbO, MoO₃.

Several methods are employed for obtaining the molybdic acid from this mineral.

I. In order to remove the carbonates of zinc and of protoxide of iron, the finely-powdered ore is treated for some time, and frequently agitated, with dilute hydrochloric acid; it is afterwards washed by decantation, and decomposed by boiling concentrated hydrochloric acid. The mixture is then evaporated to dryness, the residue powdered, and digested with ammonia. Insoluble basic chloride of lead and molybdate of ammonia are thus formed; the solution containing the latter is filtered off, and evaporated to crystallization. The mother-liquor from the crystals, or even the entire solution, may be mixed with

^{*} May be purchased very reasonably, in compact masses, of J. P. Biebel, at Garmisch, Partenkirchen, Bavaria.

nitric acid, evaporated to dryness, and the residue extracted with water, when the molybdic acid is left.

II. The powdered ore is fused with an equal weight of dry carbonate of soda, the fused mass poured out, taking care to separate it as far as possible from the oxide of lead which has settled at the bottom, and dissolved in hot water; the small quantity of lead which has been carried into solution is precipitated from the latter, while hot, by a mixture of ammonia and carbonate of ammonia, the solution filtered, acidified with nitric acid, evaporated to dryness, the nitrate of soda extracted from the mass with water, and the molybdic acid thoroughly washed.

III. In order to avoid the perforation of the crucible, which occurs frequently in this process, the ore may be fused with an equal weight of carbonized bitartrate of potassa, when the lead separates in the metallic state, without any reduction of molybdic acid taking place.

IV. The powdered ore is fused with an equal weight of calcined bitartrate of potassa and as much sulphur; the sulphomolybdate of potassa thus produced is dissolved in water, and the sulphide of molybdenum precipitated from the solution by dilute sulphuric acid. When this precipitate is washed, dried and ignited in a covered crucible, it leaves a crystalline grey sulphide, from which molybdic acid may be prepared by the method employed in treating molybdenite.

V. The finely-powdered mineral is digested, with constant stirring, with 1½ parts of concentrated sulphuric acid, until it is perfectly white. The heat is then raised to incipient volatilization of sulphuric acid, the mixture allowed to cool, and the blue pasty mass stirred up with much water, in order to separate the sulphate of lead; the solution containing the molybdic acid is decanted, filtered

and evaporated in a porcelain dish, with addition of some nitric acid, until the sulphuric acid begins to evaporate; the mixture should be constantly stirred. The molybdic acid is thus separated as a white precipitate; when the greater part of the sulphuric acid has been expelled, the mixture is diluted with water, the molybdic acid filtered off and well washed, water containing nitric acid being used towards the end. Some more molybdic acid may be obtained by evaporating the filtrate and washings. It is free from phosphoric acid.

If it contain any phosphoric acid, its ammoniacal solution, when acidified with nitric acid, and heated, becomes yellow and deposits a yellow powder.

The molybdic acid may be obtained from molybdate of ammonia by gradually heating the salt, with full access of air.

It is always obtained in a perfectly pure state by sublimation, for which purpose it is heated in a platinum crucible, which is covered with a platinum capsule kept full of water.

For quantitative analysis, the pure crystallized mineral is finely powdered, completely decomposed by digestion with nitric acid, the mixture neutralized with ammonia, and digested with an excess of sulphide of ammonium. The sulphide of lead which is thus formed, is filtered off from the dissolved molybdate, washed with dilute sulphide of ammonium, dried at 100°, and weighed. From the solution, the sulphide of molybdenum is precipitated by dilute nitric acid, collected upon a filter, dried at 100°, washed, dried and weighed. A weighed portion of it is then introduced into a bulb-tube, and heated in a stream of hydrogen until it loses no more sulphur. From the weight of the residual MoS₂, calculated for the total

amount of the precipitate, that of the molybdic acid is ascertained.

91. MOLYBDENITE.*

MoS2.

The finely-powdered mineral is roasted, with frequent stirring, in a crucible placed obliquely, as long as any odour of sulphurous acid is perceptible.

The molybdic acid which has been formed is extracted from the yellow mass thus produced, by digestion with dilute ammonia. The residue, should it still contain sulphide of molybdenum, is then again roasted.

The filtered solution is mixed with one or two drops of sulphide of ammonium, to separate the copper, the precipitate filtered off, the solution evaporated to dryness, the salt again dissolved in dilute ammonia, the solution filtered from any impurities, and evaporated to crystallization. (See Molybdate of Lead.)

The molybdic acid may also be precipitated from the solution of an alkaline molybdate neutralized with nitric acid, by basic nitrate of suboxide of mercury. The yellow precipitate is allowed to subside, filtered off, washed with a dilute solution of the mercury-salt, dried and ignited. Molybdic acid may also be quantitatively determined, by this method. The precipitate is collected upon a filter (previously dried at 100° and weighed), dried at 100°, and a weighed portion of it gently ignited in a bulb-tube, through which a stream of hydrogen is passed, when dark brown binoxide of molybdenum, MoO₂, is left.

^{*} May be obtained of Franz Holenias, at Bleiberg, where also crude molybdic acid may be purchased at a moderate price.

92. BROWN IRON-ORE, CONTAINING VANADIUM.

In order to extract the vanadium, the quantity of which does not amount even to 1 per cent, the finely-powdered ore is intimately mixed with 1 its weight of nitre, and exposed, for an hour, in a crucible, to a gentle ignition. When cool, the mass is powdered and boiled with water.

The filtered solution has a yellow colour, and contains the vanadates, chromates (molybdates?), arsenates, phosphates, nitrites and silicates of potassa and alumina.

It is gradually mixed, and well stirred, with nitric acid, taking care that it may still remain slightly alkaline and hat no nitrous acid is liberated, which would reduce the vanadic and chromic acids. The precipitate of alumina and silica thus separated is filtered off.

The solution is then mixed with an excess of solution of chloride of barium, as long as any precipitate is produced. The precipitate, consisting of the baryta-salts of the abovementioned acids, is filtered off, washed and boiled while yet moist, with dilute sulphuric acid, which must not be added in too great excess. The reddish-yellow acid filtrate is neutralized with ammonia, concentrated by evaporation, and a fragment of chloride of ammonium is placed in it. In proportion as the solution becomes saturated with chloride of ammonium, vanadate of ammonia is deposited as a white or yellow crystalline powder, which is allowed to separate completely, filtered off, and washed with a saturated solution of chloride of ammonium. When gradually heated with full access of air, it leaves dark red vanadic acid, which fuses when heated more strongly, and solidifies, on cooling, to a very crystalline mass.

The solution obtained by lixiviating the mass after

fusion with nitre, may also be mixed with sal-ammoniac, and boiled, in order to neutralize the free alkali, and to precipitate silica and phosphate of alumina. This precipitate usually contains also vanadic acid, which may be converted into sulphide by fusion with an equal weight of carbonate of potassa and sulphur; the fused mass is extracted with water, and the brown sulphide of vanadium precipitated from the filtered solution by dilute sulphuric acid.

If the iron-ore be reduced by fusion with borax (see Iron Assay), in a crucible lined with charcoal, a well-fused, crystal-line regulus of iron is obtained, which contains vanadium, chromium, arsenic, phosphorus, silicon and carbon.

Moreover, see Ash of the Refining-hearth.

93. VANADATE OF LEAD.

PbCl, PbO + 2 (2 PbO, VO_3).

There exist some varieties of this mineral, at present very rare, which contain no chloride of lead.

This mineral, when treated with nitric acid, first becomes red, then dissolves. If the solution be mixed with ammonia, and afterwards with an excess of sulphide of ammonium, sulphide of lead is precipitated, and a dark red solution obtained, from which acids precipitate the dark brown sulphide of vanadium. The precipitate is roasted in air, and afterwards converted into vanadate of potassa by fusion with a small quantity of nitre. This salt is dissolved in a little water, and vanadate of ammonia precipitated from the solution by sal-ammoniac. (See No. 92.)

The mineral is only imperfectly decomposed by sulphuric

acid. The decomposition, however, is complete if it be fused with bisulphate of potassa. On treating the mass with water, the lead remains behind as sulphate, while vanadic acid is dissolved.

94. CHROME-IRON-ORE.

FeO, Cr₂O₃.

I. For the mere qualitative separation, the very finely-powdered ore is fused for at least half an hour, at a bright red heat, with an equal weight of nitre and as much carbonate of potassa; from the fused mass, when cool, the chromate of potassa which has been produced is extracted with water.

The residue, consisting of sesquioxide of iron and variable quantities of alumina and magnesia, is dissolved in concentrated hydrochloric acid, which generally leaves some undecomposed mineral, and the three oxides are then separated as in No. 74.

The solution of chromate of potassa usually contains a little alumina, silica and manganic acid, to precipitate which it is mixed with a little carbonate of ammonia and boiled.

In order to obtain bichromate of potassa from this solution, it is acidified with nitric acid, concentrated by evaporation, and the salt allowed to crystallize out.

The chromic acid may be precipitated as chromate of lead, by neutralizing the solution with acetic acid and adding acetate of lead.

To separate the chromium as sesquioxide, the solution is acidified with sulphuric acid, sulphurous acid added till the solution has an emerald-green colour, the sesquioxide of chromium precipitated by ammonia, washed and ignited.

Or the yellow solution may be exactly neutralized with nitric acid, and the chromic acid precipitated by nitrate of suboxide of mercury. When washed, dried and ignited, the yellowish-red chromate of suboxide of mercury leaves a pure green sesquioxide of chromium.

II. Chrome-iron-ore may also be quantitatively analyzed by the above process, the fusion being conducted in a platinum crucible, though it will be found that a quantity of ore will be left undecomposed, varying according to the state of division to which it was reduced. From the solution, after neutralization with nitric acid, the chromic acid is best precipitated by nitrate of suboxide of mercury; the precipitate is washed with a dilute solution of that salt and ignited. The following method is more certain.

The mineral, which should be powdered as finely as possible and weighed, is fused, in a platinum crucible, with 4 times its weight of bisulphate of potassa, care being taken that the mass, which froths up at first, may not run over the side of the crucible. Ultimately, it is heated to redness, and retained in fusion, at a red heat, for a considerable time. The salts formed are sparingly soluble in water and acids; the sesquioxide of chromium must therefore be converted into alkaline chromates, for which purpose there is added to the cooled mass, in the crucible, about twice its volume of a mixture of equal parts of nitre and carbonate of soda. The mass is then heated to complete fusion.

On cooling, the chromate of potassa is extracted with hot water, the residue of sesquioxide of iron, alumina and magnesia, thoroughly washed, dissolved in concentrated hydrochloric acid, and analyzed as in No. 74. The solution of chromate of potassa is acidified with hydrochloric acid, heated to ebullition, and alcohol added to the boiling solution until it has acquired an emerald-green-colour, when the sesquioxide of chromium is precipitated by ammonia, ignited and weighed.

95. CHROMATE OF LEAD.

PbO, CrO₃.

(Chrome-yellow, often adulterated with white clay, with BaO, SO₃,—CaO, CO₂,—CaO, SO₃, or with PbO, SO₃.)

I. Pure chromate of lead should give the quantities of oxide of lead and chromic acid calculated from the formula.

For analysis, it is digested with a mixture of fuming hydrochloric acid and alcohol, when a green solution of sesquichloride of chromium is produced, the lead remaining undissolved as a white chloride. The latter is collected upon a filter dried at 100°, washed with alcohol, and dried at 100°. The acid solution is diluted with water, evaporated to expel the alcohol, and the sesquioxide of chromium precipitated by ammonia; the liquid is heated to ebullition, the precipitate filtered off, ignited and weighed.

II. For the mere qualitative analysis of a specimen of chrome-yellow mixed with the substances mentioned above, it is treated as before, with alcohol and hydrochloric acid, as little as possible of the latter being employed, in order that the clay may remain untouched.

From the solution, the sesquioxide of chromium is precipitated by ammonia; it always, however, carries down some lime.

In order to separate them accurately, they must be precipitated together, from the hot solution, by a mixture

of ammonia and carbonate of ammonia. After drying, the precipitate is fused with 3 times its weight of a mixture of carbonate and nitrate of potassa, and the fused mass treated with water, which dissolves the chromate of potassa, and leaves the carbonate of lime.

Or the precipitate, while yet moist, may be digested with hypochlorite of soda, which dissolves the sesquioxide of chromium, as chromate of soda, leaving the carbonate of lime undissolved. The solution is then heated to ebullition, in order to decompose any bicarbonate.

From the residue, which may consist of the sulphates of lime, baryta and lead, the first may be entirely extracted by washing with water, or with a solution of common salt or of sal-ammoniac, in which it is far more soluble. In the solution, either the sulphuric acid is precipitated, by a baryta-salt, or the lime by an oxalate.

The sulphate of lead is extracted from the residue by digestion with tartrate of ammonia containing free ammonia, and the lead precipitated from the solution by sulphuretted hydrogen or chromate of potassa.

The mixture of clay and sulphate of baryta which remains at last, is heated with concentrated sulphuric acid until the greater excess of the latter has been expelled, when the sulphate of alumina is extracted with water, and the alumina precipitated by ammonia.

In order to extract the silica from the residue, which contains also sulphate of baryta, it is boiled in a concentrated solution of carbonate of soda, in which the silica is dissolved and may be reprecipitated by sal-ammoniac. The residue consists of carbonate of baryta mixed with more or less undecomposed sulphate of baryta. (See No. 14.)

A good method of determining the amount of chromic acid (and therefore of chromate of lead) contained in a

specimen of commercial chrome-yellow, consists in reducing the chromic acid to the state of sesquioxide of chromium by means of oxalic acid, and in determining the quantity of carbonic acid produced.

This may be effected in the same way as the testing of manganese-ores in an apparatus arranged for the quantitative determination of carbonic acid, the weighed chromate of lead being mixed with oxalate of potassa, and sulphuric acid allowed to flow upon it. 10 parts by weight of carbonic acid indicate 7.6 parts of chromic acid, or 24.5 of pure chromate of lead. Hence, 100 parts of pure chromeyellow should give 40.4 of carbonic acid.

96. PITCH-BLENDE.

UO, U2O3,

(together with various extraneous substances, in variable quantities, including silica, iron, nickel, cobalt, zinc, copper, bismuth, lead, manganese, arsenic, antimony, sulphur, lime and manganese; sometimes also selenium and vanadium.)

PREPARATION OF PURE SESQUIOXIDE OF URANIUM.— The finely-powdered ore is digested with moderately dilute sulphuric acid, with gradual addition of nitric acid, until it is converted into a white powder, and partly dissolved. The greater excess of sulphuric acid is then evaporated, the mass digested with much water, and the cold solution, after subsidence of the residue, filtered off.

This residue consists of silica, sulphate of lead and basic sulphate and arsenate of bismuth.

The solution is then heated to about 60°, and sulphuretted hydrogen-gas passed through it, at this temperature,

for some time; the solution is afterwards allowed to cool while the gas is still passing, and, when fully saturated, set aside in a covered vessel for twenty-four hours. The sulphuretted hydrogen is then expelled by a gentle heat, and the precipitate filtered off.

The precipitate contains arsenic, antimony, copper, and the rest of the lead and bismuth.

The solution is then heated to ebullition, and fuming nitric acid gradually added to the boiling liquid, until all the protoxide of iron is reconverted into sesquioxide, and the solution has acquired a pure yellow colour. It is then precipitated by an excess of ammonia, and the yellowish-brown precipitate filtered off.

Part of the nickel, cobalt, zinc, lime and magnesia remain in solution, but the remainder is precipitated together with the sesquioxides of uranium and iron.

The washed precipitate is treated with a hot, pretty strong solution of carbonate of ammonia containing free ammonia, with which the precipitate is digested, at a moderate heat, until it has the appearance of hydrated sesquioxide of iron. The solution of uranium is rapidly filtered off, while hot, and the residue of hydrated sesquioxide of iron (still containing uranium) is washed, the washings being received apart from the filtrate.

The solution (which is yellow, or coloured reddish by the cobalt) deposits on cooling, if sufficiently concentrated, crystals of the pure double carbonate of ammonia and sesquioxide of uranium, which may be collected, and washed several times with cold water. When ignited, this salt leaves pure dark green proto-sesquioxide of uranium.

The mother-liquor is mixed with the washing-water, and sulphide of ammonium carefully added, drop by drop, as

long as it produces a dark brown precipitate, which is immediately filtered off.

The precipitate consists of the sulphides of cobalt, nickel and zinc.

The yellow filtrate is then boiled till the greater part of the ammoniacal salt is volatilized, and all the sesquioxide of uranium precipitated.

The pure yellow precipitate, uranate of ammonia is filtered off, and, when the filtrate begins to pass through turbid, washed with solution of sal-ammoniac.

When ignited, it leaves dark green proto-sesquioxide of uranium. By digesting this with dilute hydrochloric acid, any lime and magnesia may be extracted.

In order to prepare protoxide of uranium from the uranate of ammonia, it is dissolved in hydrochloric acid, the solution mixed with an excess of pure sal-ammoniac, and about an equal quantity of pure common salt; it is then evaporated to dryness, and the mass heated in a covered crucible until the sal-ammoniac is volatilized, and, lastly, until the common salt fuses. On dissolving it in water the protoxide of uranium is left as a hard crystalline powder. The common salt only serves to shield the oxide from the action of air.

In order to extract from the hydrated sesquioxide of iron the small quantity of sesquioxide of uranium which is chemically combined with it, it is dissolved in the smallest possible quantity of hydrochloric acid, the solution neutralized with carbonate of ammonia, and added, drop by drop, with constant stirring, to a mixture of carbonate of ammonia and sulphide of ammonium, when all the iron is separated as sulphide, and the sesquioxide of uranium remains in solution; the latter may be precipitated by boiling the filtrate.

Or the sesquioxide of iron may be reduced in a stream of hydrogen, and the reduced pyrophoric mass allowed to fall, immediately, into dilute hydrochloric acid, which dissolves the iron, leaving the uranium as protoxide.

In order to detect selenium, arsenic and vanadium in pitch-blende, it is ignited with \(\frac{1}{4} \) its weight of a mixture of carbonate of soda and nitre. The selenates, vanadates and arsenates of the alkalies may then be extracted with water.

97. SELENIFEROUS DEPOSIT FROM THE SULPHURIC-ACID CHAMBERS.**

(Sulphate of lead, selenium, selenide of mercury, selenates and selenites, &c.)

The dry mass is rubbed to a thin paste with a mixture of about equal parts of sulphuric acid and water, and boiled for a long time, concentrated nitric acid or chlorate of potassa being added at intervals, to oxidize the free selenium, until all the reddish colour has disappeared.

The mixture is then diluted with water and filtered. The solution contains, besides iron, copper, mercury and a little lead, all the selenium as selenous and selenic acids. It is mixed either with about as much common salt as amounts to half the weight of the deposit originally employed, or with $\frac{1}{4}$ of its volume of crude fuming hydrochloric acid, and boiled down to about $\frac{1}{4}$ of its original bulk. The hydrochloric acid reduces the selenic acid to selenious acid.

On cooling, the solution is poured off from any sulphate of potassa and common salt which may have been depo-

^{*} To be obtained from the "Communion Schwefelsäure-Niederlage," at Goslar in the Hartz.

sited; these are washed several times with water, and the solution saturated with sulphurous acid gas, evolved from a mixture of powdered charcoal and concentrated sulphuric acid.

The selenium is thus precipitated of a fine red colour. Its separation is promoted by digestion, and ultimately by boiling for a quarter of an hour, when it becomes black, and collects into a dense hard mass. It is well washed and dried.

The filtered liquid is boiled once more with hydrochloric acid, and again treated with sulphurous acid, in case it should still contain selenium.

The selenium thus obtained contains still small quantities of lead, copper and iron, and especially mercury. On distilling it in a small retort or bent tube closed at one end, the first-mentioned impurities are left behind as selenides.

In order to free it from mercury, the distilled selenium is dissolved in *aqua-regia*, the greater excess of acid evaporated, so that no nitric acid may remain, the solution mixed with excess of carbonate of soda, evaporated to dryness, and the saline mass ignited to expel the mercury.

The mass is redissolved in water, the solution boiled with hydrochloric acid, and the selenium again precipitated by sulphurous acid.

Or the ignited mass may be mixed with about an equal weight of chloride of ammonium, and heated in a retort till the greater part of that salt has sublimed, when the selenium is reduced, and remains behind on dissolving the saline mass in water.

The selenium may also be at once extracted, and obtained free from mercury, by fusing the deposit with an equal weight of carbonate of soda and about \(\frac{1}{4}\) of nitre, in a crucible. When the mass is in a state of tranquil fusion, it is poured

out, so as to leave the oxide of lead, as far as possible, at the bottom of the crucible. It is then dissolved in water, the solution acidulated with sulphuric acid, the precipitated sulphate of lead filtered off, and the filtrate treated, as above, with hydrochloric acid and sulphurous acid. It is necessary in this process that all the nitric acid from the nitre should either be expelled or decomposed, for otherwise part of the selenium will escape precipitation.

98. SELENIDE OF LEAD.

PbSe.

The analysis is best effected, like that of fahl-ore (No. 57), by means of chlorine-gas. After the decomposition, the bulb is again weighed, in order to ascertain the amount of lead present. The greater part of the selenium is volatilized in the form of the solid chloride; only a small quantity of the liquid chloride passes over at first. These are conducted into water, which is afterwards saturated with chlorine, in order to convert all the selenious acid into selenic acid; the latter is then precipitated by chloride of barium, and the selenium determined as selenate of baryta; 100 parts of the latter correspond to 28·2 of selenium.

If the metallic selenides are mixed or combined with the metallic sulphides, as, for example, in the native selenide of mercury which contains sulphide of mercury, the sulphuric acid and selenic acid formed in the analysis are precipitated together by chloride of barium, the precipitate ignited and weighed. A weighed quantity is then heated in a bulbtube, through which a stream of dry hydrogen is passed,

when the selenate of baryta is reduced, with great facility, to the state of selenide of barium, while the sulphate of baryta remains unaltered. The selenide of barium is then extracted with dilute hydrochloric acid.

In the same way the other metallic selenides which occur as minerals may be analyzed, viz., the selenide of silver and lead, the selenide of cobalt and lead, and the selenide of mercury and lead.

In order to obtain the selenium from the selenide of lead occurring in many places in the Hartz, the mineral is powdered, treated with dilute hydrochloric acid to remove the calcareous spar and spathic iron-ore, well washed and dried. It is then very intimately mixed with an equal weight of carbonate of potassa containing charcoal (calcined bitartrate of potassa), covered with coarse charcoal-powder in a crucible, the cover of which is then luted on, and exposed for an hour to a moderate red heat. When cool, the mass, which contains all the selenium as selenide of potassium, is quickly powdered in a warm mortar, thrown on a filter, and washed with well-boiled hot water, as long as the washings are coloured; during this operation, the funnel should always be kept full of water, so that the mass may not come in contact with the air.

The yellowish-red solution of selenide of potassium begins immediately to deposit upon its surface a film of selenium, the whole of which separates, after some days, in the form of a thin reddish-black crust; only a small quantity remains in solution in an oxidized state. It may afterwards be precipitated by heating the solution with sulphurous and hydrochloric acids.

Since selenide of lead frequently contains selenide of silver, the carbonaceous mass remaining after the extraction of the selenide of potassium may be fused with carbonate of potassa and some nitre. A metallic button of argentiferous lead is thus obtained, from which the silver may best be separated by cupellation.

99. SILVER ASSAY.

From argentiferous galena, fahl-ore, copper- and ironpyrites, &c., even when intimately mixed with gangue, the whole of the silver, concentrated in a small quantity of lead, may be extracted in the following manner:

One hundred grms. of galena, finely powdered, are fused with 30 grms. of nitre and 100 grms. of litharge.

Or 1 part of the ore is fused together with 30 to 50 parts of litharge.

Or 1 part of ore may be fused with 3 parts of anhydrous acetate of lead and 2 parts of potashes, under a layer of common salt.

In the button of lead obtained, the silver is determined by cupellation, or in the moist way.

100. IRON ASSAY.

The weighed iron-ore, in the state of fine powder, roasted or not, as the case may be, is mixed with dried borax, and the mixture exposed for an hour, in a crucible lined with charcoal, to the most intense heat of a wind-furnace with a good draught; the quantity of borax varies according to the nature of the iron-ore. The greater the quantity of extraneous matter which is present, the more borax it requires. For 10 grms. of iron-ore, 3 grms. of borax may be taken as the minimum, 10 grms. as the maximum. In

a well-conducted assay, all the iron is found reduced to a single well-fused button.

101. WET ASSAY OF IRON.

The process for determining in the moist way with great accuracy, and without a complete analysis, the amount of iron contained in an ore, consists in ascertaining the number of measures of a solution of permanganate of potassa of known strength which may be decolorized by the solution of protoxide of iron obtained from a given quantity of the ore.*

One equiv.=1.980 grms. of crystallized permanganate of potassa converts the protoxide of iron from 10 equivs.= 3.500 grms. of pure iron into sesquioxide.

So that if 19.80 grms, of the salt be dissolved in 1 litre (=1000 grms, or 1000 cub, cent.) of water; 100 cub, cent. of this solution will correspond to 3.50 grms, of iron. It must be kept in a well-stopped bottle.

An equivalent quantity (say 3.5 grms., or half that amount) of the ore to be tested is dissolved in concentrated hydrochloric acid, in a capacious flask, by the aid of heat.

* To prepare the permanganate of potassa, 8 parts of very finely-powdered manganese-ore are mixed with 7 parts of chlorate of potassa, the mixture saturated with a very concentrated solution of 10 parts of hydrate of potassa and the wet mass gradually heated in an earthen crucible to dull redness, so that it cinders together, but does not fuse. When cool, it is powdered, treated, in a flask, with a considerable quantity of hot water, and boiled until the colour of the solution has changed to a pure purple-red. It is then allowed to stand for twelve hours, the clear solution poured off from the binoxide of manganese which is deposited, and evaporated to the point of crystallization.

If the insoluble residue of foreign matters, such as clay, silica, &c., be not very considerable, it is unnecessary to filter the solution. The iron must now be entirely reduced to the state of protoxide, either by mixing the solution with several times its volume of a saturated solution of sulphurous acid, and boiling so long as any trace of that gas is perceptible; or better, by allowing a piece of zinc, free from iron, to remain in the liquid until its colour is changed to a pale green. It is then decanted from the zinc, the latter thoroughly rinsed, the solution diluted with the washing-water, and mixed with some more hydrochloric acid; the solution of permanganate of potassa is then dropped in from a burette (see Alkalimetry), until the yellow colour which the solution then acquires is changed to a clear red by adding another drop of the permanganate. The number of cubic centimeters of the manganese-solution which have been employed, at once indicates the percentage of iron in the ore.

Instead of the crystallized permanganate of potassa, the crude solution originally obtained in the preparation of that salt may be employed, provided it be first graduated—that is, quantitatively tested as to its oxidizing power. For this purpose, 3.5 grms. (or half that quantity, 1.75 grms.) of pure iron-wire are dissolved in a capacious flask by concentrated hydrochloric acid, with the aid of heat. The solution is diluted with several times its volume of cold water, and the solution of permanganate dropped into it, as directed above. When the quantity of solution employed has been read off, the whole is diluted with so much water, that 100 cub. cents. may correspond to 3.5 grms. It must be kept in a well-stopped bottle.

102. CAST-IRON.

For the detection and estimation of the foreign substances, the total weight of which does not usually exceed 5 per cent, it is best to employ separate portions of iron.

I. Carbon.—The total amount of carbon may be determined by burning the iron, in the state of very fine filings, with the aid of a slow stream of pure oxygen, as in organic analysis; the carbonic acid which is produced being collected in a weighed potassa-apparatus.

Another quantity of the iron-filings is dissolved in dilute sulphuric acid, when the combined carbon is evolved in combination with hydrogen, while the graphite is left undissolved. In this operation, the gas may be conducted through a solution of acetate of lead, when the presence of sulphur is indicated by the precipitation of sulphide of lead.

The residue insoluble in the acid is well washed, dried at 200°, and burnt, as above, in oxygen-gas. From the amount of carbonic acid, that of the graphite is calculated.

II. Silicon.—The residue from the first carbon-determination, which contains all the silicon in the form of silicic acid, is dissolved in concentrated hydrochloric acid, the solution evaporated to dryness on the water-bath, the mass digested with dilute hydrochloric acid, and the silicic acid filtered off.

III. PHOSPHORUS.—From the solution filtered from the silica, the phosphoric acid is separated as in No. 20. If the iron contain arsenic, it is obtained as arsenic acid, together with the phosphoric acid.

The amount of phosphorus may be less accurately determined by heating the fine iron-filings to redness with 2 parts of nitre and 1 part of carbonate of soda, extracting the mass with water, acidifying the solution with hydrochloric acid, and adding excess of ammonia and sulphate of magnesia.

IV. Arsenic.—The presence of arsenic may be detected by dissolving the iron in dilute sulphuric acid, filtering off the black residue, and digesting it with sulphide of ammonium. From the filtered solution, dilute sulphuric acid precipitates the pentasulphide of arsenic. The precipitate is dissolved in aqua-regia, the nitric acid expelled by evaporation, and the arsenic reduced in Marsh's apparatus.

The solution of iron filtered from the black residue is neutralized with carbonate of soda, mixed with a few drops of sesquichloride of iron, and then with acetate of soda, when arseniate of sesquioxide of iron is precipitated, which may be easily decomposed by sulphide of ammonium.

For the quantitative determination of the arsenic, the cast-iron is dissolved in hydrochloric acid, with gradual addition of nitric acid, the solution filtered from the carbon, and heated with sulphurous acid till all the sesquichloride of iron is converted into protochloride; the excess of sulphurous acid is then expelled by heat, and the solution saturated with sulphuretted hydrogen, and allowed to stand for twenty-four hours in a closed vessel; the excess of gas is afterwards evaporated, and the precipitate filtered off.

V. COPPER.—This metal is contained in the precipitate produced as above, by sulphuretted hydrogen. After drying, it is distilled in a tube, when sulphide of copper remains behind. Or the sulphide of arsenic may be dissolved out by solution of potassa, or more completely, by solution of monosulphide of potassium.

VI. Manganese.—The solution filtered from the precipitate produced by sulphuretted hydrogen, in V, is heated

to the boiling-point, and the protoxide of iron entirely converted into sesquioxide by adding chlorate of potassa or hypochlorite of soda. The oxide of manganese and sesquioxide of iron are then separated from each other by means of bicarbonate of soda, as in No. 23.

VII. Aluminum.—The alumina is contained in the sesquioxide of iron which is then precipitated, and may be separated from it as in No. 19.

VIII. Magnesium and Calcium remain, together with the protoxide of manganese, in the solution filtered from the precipitate produced by bicarbonate of soda. (See No. 23.)

IX. Chromium and Vanadium.—A large quantity of the iron-filings is ignited with 2 parts of nitre and 1 part of carbonate of soda, the mass extracted with water, and the solution treated as in No. 92, when phosphoric and arsenic acids may likewise be sought. It is safer to employ for this purpose the carbonaceous residue obtained by dissolving a large quantity of the iron in dilute sulphuric acid.

X. Molybdenum.—Sometimes this metal is extracted, together with the arsenic, by sulphide of ammonium, from the black carbonaceous residue; in such a case, it is reprecipitated, together with the pentasulphide of arsenic, on adding an acid to the solution. If this precipitate be distilled in a tube, the sulphide of molybdenum is left behind.

XI. Sulphur.—The sulphur may be determined approximately by evolving it as sulphuretted hydrogen, as in No. 1, when the iron is dissolved in dilute sulphuric acid. Or it exists as sulphuric acid in the solutions obtained at III, and VI, and may be precipitated by chloride of barium. Or a large quantity of iron may be dissolved in aqua-regia, and the sulphuric acid formed may by precipitated from the diluted solution by chloride of barium.

XII. NICKEL AND COBALT may be detected in the solution from which the copper has been removed by sulphuretted hydrogen. This solution is re-oxidized, and the sesquioxide of iron precipitated by carbonate of baryta, after which the nickel and cobalt are precipitated by sulphide of ammonium.

For the detection of most of the admixtures, it is best to employ the black residue which is left on dissolving the iron in dilute sulphuric acid, and which can easily be prepared in considerable quantity. It contains silicic acid, carbon, carbide of iron, phosphide of iron, arsenide of iron, compounds of chromium and vanadium with iron, molybdenum, &c.

The total amount of the carbon (phosphorus, arsenic, chromium, &c.?) in iron may be separated by digesting the fine iron-filings with a solution of chloride of copper, when all the uncombined iron is dissolved, and copper precipitated in its stead. When the solution has been poured off, the precipitated metal is digested, out of contact of air, with a neutral solution of sesquichloride of iron which redissolves the metallic copper.

When this residue is digested with potassa, the latter dissolves a newly formed brown humus-like substance, together with phosphoric acid, arsenic acid, and silicic acid. Almost the whole of the silicic acid may be determined in this residue.

It is yet to be ascertained whether this residue can be analyzed by heating in chlorine-gas.

103. ASH OF THE REFINING-HEARTH.

Crystallized = 3 FeO, SiO₃.

The analysis of pure crystals picked out of the mass is simple and easy, since they consist essentially only of protoxide of iron and silicic acid. They are finely powdered, and treated with hydrochloric acid and some concentrated nitric acid until they are completely gelatinized, the analysis being conducted as in the case of Lievrite. The sesquioxide of iron obtained is calculated as protoxide.

The quantitative analysis of the ordinary compact slag is far more difficult and complex, since it may contain, in addition to the above principal constituents, small variable quantities of the protoxides of copper, nickel, cobalt and manganese, beside the oxides of chromium, molybdenum and vanadium, together with alumina, potassa, lime, magnesia, arsenic and phosphoric acids.

Several of these constituents can only be discovered by a qualitative analysis, for which a large amount of slag is employed. The process is conducted as follows:

A pound of the slag, powdered as finely as possible, is intimately mixed with an equal weight of nitre, and as much carbonate of potassa,* and exposed for an hour, in a crucible, to a moderate red heat. The mass is finely powdered, boiled out with water, the solution filtered off, and the residue washed several times with hot water.

The solution may contain, besides alkaline carbonates and nitrites, vanadic acid, chromic acid, molybdic acid, phosphoric acid, silicic acid and alumina. A yellow colour indicates the presence of chromic acid.

^{*} Perhaps smaller quantities of both might be employed.

It is now carefully mixed with nitric acid, so that it may still remain alkaline, and any silica which may be precipitated is filtered off. A yellow colour at this stage of the process bespeaks the presence of vanadic acid. The liquid is then evaporated to crystallization, and the greater part of the alkaline nitrate allowed to crystallize out in as cool a place as possible. The mother-liquor is poured off from the crystals, which are washed several times with a little perfectly cold water; the washings are mixed with the mother-liquor, and acetate of lead added as long as any precipitate is produced. This precipitate contains all the substances above enumerated, in combination with oxide of lead. It is filtered off and washed once or twice.

Chromic and vanadic acids cannot be completely separated from oxide of lead by means of sulphuric acid. The precipitate is therefore treated, while still moist, with a mixture of fuming hydrochloric acid and strong alcohol, with which it is heated nearly to ebullition, when all the lead and silica are separated in an insoluble state, and the metallic acids are converted into green chlorides, and dissolved together with the phosphoric and arsenic acids. The chloride of lead is filtered off and washed with alcohol; the green solution is evaporated to the consistency of a syrup, mixed with a slight excess of a concentrated solution of potassa, and chlorine passed into it until the metallic oxides have redissolved in the form of acids, imparting a yellow colour to the solution.* The liquid is then neutralized with ammonia, concentrated as far as possible by evaporation, allowed to cool, and a fragment of chloride of ammonium placed in it, so large as not to be entirely dissolved. The vanadic acid is thus almost completely precipitated as an

^{*} Phosphate of alumina may precipitate here, and must be analyzed separately. (See No. 13.)

ammonia-salt, in the form of a white or yellow crystalline powder. After twenty-hours it is filtered off and washed, first with a saturated solution of sal-ammoniac, afterwards with alcohol. It may be purified by dissolving in boiling water with the addition of some ammonia.*

When dry, it is very gradually heated in a shallow platinum dish to expel the ammonia, and the residual vanadic acid is fused at a low red heat. If pure, it solidifies, on cooling, to a dark brown-red, very crystalline mass.

The solution filtered from the vanadate of ammonia is mixed with ammonia, and afterwards with a solution of chloride of magnesium, which precipitates all the phosphoric, and most of the arsenic acid. After twenty-four hours, the precipitated double salts are filtered off, washed with dilute ammonia, dissolved in hydrochloric acid, the solution heated to 50°, and the arsenic precipitated by a stream of sulphuretted hydrogen-gas. In the filtrate from the sulphide of arsenic, the phosphoric acid may again be precipitated as a double salt by adding ammonia.

The solution filtered from the magnesia-precipitate, which still contains the chromic and molybdic acids, is saturated with sulphuretted hydrogen and heated, when all the chromium is precipitated as green sesquioxide.

From the solution filtered from this precipitate, the molybdenum is precipitated by dilute sulphuric acid as a

* It is possible that, if molybdenum be present, a yellow compound of phosphoric acid, molybdic acid and ammonia might be precipitated here. It is insoluble in hot dilute nitric acid. This circumstance might be made use of for separating the molybdic acid at once from the solution after treatment with chlorine. The solution would be mixed with ammonia, and afterwards boiled, with addition of nitric acid in slight excess, when the compound would separate as a yellow powder. It contains 3 per cent of phosphoric acid.

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brown sulphide of molybdenum, from which, when heated in a tube, a mixture of sulphur and sulphide of arsenic sublimes, while black lustrous MoS₂ remains behind.

The residue of sesquioxide of iron which is left after ignition with nitre and alkali, and extraction with water, is partly dissolved by digestion with concentrated hydrochloric acid, and if sulphuretted hydrogen be passed through the solution, the copper will be precipitated.

The solution filtered from the precipitate is heated to the boiling-point, and a sufficient quantity of chlorate of potassa gradually added, to convert the protochloride of iron into sesquichloride. The small quantities of nickel, cobalt and manganese which are present may be detected by precipitating the solution either with excess of ammonia or with carbonate of lime, when those metals remain in solution, and may be precipitated by sulphide of ammonium.

104. GLASS.

Silicates of CaO, and KO or NaO, frequently also, of PbO.

Two analyses are made, one by fusion with an alkaline carbonate, for the determination of silicic acid; the other by decomposing the glass with hydrofluoric acid, in order to estimate the alkali.

I. The very finely-powdered glass is fused with 3 times its weight of carbonate of potassa and soda (No. 10), the mass softened in water, dissolved in dilute hydrochloric acid, evaporated to dryness, redissolved in water, acidulated with hydrochloric acid, the silica filtered off and washed.

From the solution, the small accidental impurities of

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sesquioxide of iron, oxide of manganese, and alumina, which are usually contained even in white glass, are precipitated by ammonia, after the solution has been mixed with some chlorine-water to peroxidize the protoxide of manganese.

The lime is afterwards precipitated by oxalic acid, and the solution filtered from the oxalate of lime is tested for magnesia, which may, moreover, have been precipitated with the alumina.

If the glass contain oxide of lead, that metal is precipitated by sulphuretted hydrogen from the solution filtered from the silicic acid.

II. For the determination of alkalies, a second quantity of the very finely-powdered glass is decomposed by hydrofluoric acid, or by ignition with carbonate of baryta, as in the analysis of feldspar, the subsequent process being also conducted as in that analysis, so that the other bases may, if necessary, be again determined here.

105. CLAY.

3 Al₂O₃, 4 SiO₃+6 HO, with variable quantities of KO, MgO, FeO, MnO, Feldspar, Sand, &c.

The water is determined by igniting the clay previously dried at 100°.

I. The clay is heated with concentrated sulphuric acid, the greater excess of acid evaporated, the residue dissolved in concentrated hydrochloric acid, by the aid of heat, and the silicic acid filtered off. If the clay contain an admixture of sand or feldspar, the silica is dissolved in a boiling concentrated solution of carbonate of soda, when the sand and feldspar remain undissolved.

The hydrochloric solution is considerably diluted, and

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gradually neutralized with carbonate of soda, so that sesquioxide of iron and alumina are precipitated, while protoxide of manganese, lime and magnesia remain in solution as bicarbonates. The separation of alumina and sesquioxide of iron is then effected as in No. 19, that of the other bases as in No. 23.

II. The clay is fused with 3 times its weight of carbonate of potassa and soda (see No. 10), the fused mass dissolved in dilute hydrochloric acid, the solution evaporated to dryness, the residue dissolved in water containing hydrochloric acid, and the solution filtered off.

The separation of the other bases contained in the solution is then effected as in I.

III. For the determination of the alkali, a separate portion of the clay is decomposed by fusion with hydrate or carbonate of baryta, and the process conducted as in No. 73, the baryta and the other bases being precipitated from the solution by a mixture of ammonia and carbonate of ammonia; after gently heating, the precipitate is filtered off, the solution evaporated, and the residue ignited, when chloride of potassium and chloride of sodium are left. Or the analysis may be made with hydrofluoric acid, as in No. 73.

106. COMMON LIMESTONE, HYDRAULIC LIMESTONE, MARL.

Carbonates of CaO, MgO, FeO, MnO, with Clay containing alkali, and sometimes 3 CaO, ${\rm PO}_5$.

I. For the detection of the alkali, large fragments of the mineral, when it contains carbonate of lime in predominating quantity, are placed in a charcoal fire, and heated

for half an hour to whiteness, when the clay, which contains the alkali, is decomposed.

The ignited mass is carefully freed from adhering ash, powdered, exhausted with water, the solution mixed with some carbonate of ammonia, evaporated, the precipitated carbonate of lime filtered off, the solution acidified with hydrochloric acid, evaporated to dryness, and the residual chloride of potassium or sodium heated to dull redness. If both salts be present, they are separated by bichloride of platinum.

II. From a portion of the mineral which has been dried at 100° and weighed, the water is expelled by ignition in a glass tube, and its quantity determined by collecting it in a

weighed chloride-of-calcium-tube.

III. The carbonic acid may be expelled from another portion of the mineral by nitric acid in the apparatus employed for testing potashes, and its amount determined directly by the loss of weight.

Or a weighed quantity of the substance is fused with about 4 parts, accurately weighed, of vitrified borax, in a platinum crucible, when all the carbonic acid is expelled, and its amount may be determined from the loss of weight, if the water expelled at the same time be taken into account in the calculation. (See No. 7.)

IV. Another very finely-powdered portion is digested with very dilute nitric acid, which dissolves the carbonates, together with the phosphate of lime, leaving the clay, which is filtered off, ignited and weighed. It is then analyzed as in No. 105.

The separation of the other constituents present in the solution is effected as in No. 13.

107. IODIDE, BROMIDE, AND CHLORIDE OF SODIUM.

The solution is mixed with nitrate of protoxide of palladium, when all the iodine is precipitated as dark brown iodide of palladium, the bromide of palladium remaining in solution because chloride of sodium is present. After the lapse of twelve hours, the precipitate is collected upon a weighed filter, dried over oil of vitriol, or at a temperature not exceeding 80°, and weighed.

The excess of palladium in the filtrate is separated by means of sulphuretted hydrogen, in order to prevent the formation of a precipitate containing palladium upon the subsequent addition of nitrate of silver. The excess of sulphuretted hydrogen is then removed from the solution by sulphate of sesquioxide of iron, and the filtrate mixed with nitrate of silver, when a precipitate of chloride and bromide of silver is formed, which is collected, washed, dried and fused. A quantity of this precipitate, weighed in a bulb-tube, is fused in a current of dry chlorine until bromine vapour ceases to be evolved, and the tube changes no longer in weight. Before weighing, every trace of chlorine must be removed from the bulb.

A simpler method consists in pouring water over the weighed mixture of bromide and chloride of silver, adding a few drops of hydrochloric acid, and a fragment of zinc. In twenty-four hours the silver is completely reduced; it is rubbed to powder, boiled with water containing hydrochloric acid, afterwards washed with pure water, ignited and weighed.

The difference between the equivalents of chlorine and bromine is to the equivalent of bromine, as the difference between the amounts of chloride and bromide of silver employed, and the amount of chloride which the reduced silver ought to yield, is to the amount of bromine present.

For example: 200 parts of a mixture of equal weights of chloride and bromide of silver gave, when reduced, 132.73 of silver, which would yield 176.31 of chloride of silver.

Difference between the equivalents of chlorine and bromine = 44.5. Difference obtained = 23.69. Then 44.5:80=23.69:x (=42.5 bromine).

By the same indirect method, the amount of iodine contained in a mixture of iodide with chloride or bromide of sodium may be determined.

The iodine may also be determined in a mixture of chloride and iodide of potassium or sodium, by adding a solution of sulphate of copper mixed with sulphurous acid, when the iodine is precipitated as white subiodide of copper, which is then washed.

This method is also applicable for the approximative separation of iodine and bromine.

108. CRUDE COMMON SALT.

- I. A weighed quantity of the moist salt is dried for some time at about 100°, then heated to about 300° in a covered crucible, and the water determined from the loss.
- II. For the estimation of the sulphuric acid, the salt is dissolved in water (when any insoluble impurities are left),

the solution slightly acidified with hydrochloric acid, and precipitated by chloride of barium.

III. The lime is determined in a larger quantity of the salt, by precipitating it from its solution by oxalate of ammonia, and filtering off the oxalate of lime when it has subsided.

IV. The filtrate is concentrated by evaporation and mixed with ammonia and phosphate of soda to precipitate the magnesia; after the lapse of twenty-four hours, the precipitate is filtered off and washed with ammonia.

V. The very small quantity of potassa which is usually present, may be detected by concentrating the solution of a large quantity of the salt so that a great part of the chloride of sodium may crystallize out; the potassium is then precipitated from the mother-liquor with bichloride of platinum.

VI. The bromine may be detected by passing chlorine into the mother-liquor obtained from a large quantity of the saline solution, and agitating the liquid with ether, which takes up the bromine, and thence acquires a yellow colour. The bromine may then be converted into bromide of ammonium by adding ammonia.

VII. In order to detect the iodine, the mother-liquor is mixed with some starch-paste, and weak chlorine-water added drop by drop; or the vapour of bromine or of nitrous acid may be allowed to flow on to the surface of the mixture.

For the quantitative determination of iodine and bromine, see No. 107.

109. INCRUSTATIONS FROM SALT-PANS.*

I. A weighed portion is heated nearly to redness in order to determine the water.

II. Another portion is finely powdered and boiled with water, the residual carbonates of lime and magnesia filtered off, washed with hot water, and the two bases separated as in No. 12. This residue sometimes contains iron and manganese.

III. The filtrate is mixed with chloride of ammonium, and the lime precipitated by oxalate of ammonia. (See No. 12.)

IV. The solution filtered from the precipitate is mixed with ammonia, and the magnesia precipitated by phosphate of soda. (See No. 6.)

V. Another portion of the incrustation is dissolved in hot dilute hydrochloric acid, and the sulphuric acid precipitated by chloride of barium (No. 3).

VI. A smaller quantity is dissolved in dilute nitric acid, and the chlorine precipitated by nitrate of silver (No. 1).

VII. The sodium and soda are calculated from the loss.

VIII. In order to detect a small quantity of sulphate of potassa, a large quantity of the incrustation is finely powdered, boiled with an excess of hydrate of baryta, the

^{*} Easily obtained at the salt-works.

solution filtered off, the lime and baryta precipitated by a mixture of ammonia and carbonate of ammonia, the filtrate acidified with hydrochloric acid and evaporated to dryness; the residue is ignited, dissolved in water, and the solution treated with bichloride of platinum.

In this process also, the soda which previously existed as sulphate, may be obtained in the form of carbonate.

110. MINERAL WATERS, WELL-WATERS, SALINE SPRINGS.

It is supposed that the analyst has an unlimited quantity of water at his disposal, so that separate portions may be employed for the determination of most of the individual constituents. For the estimation of those substances which are present in large quantity, small portions of water must be employed, larger quantities being taken for such constituents as exist in small proportion.

I. The *specific gravity* is first determined, in order to ascertain, by calculation, the weight of 10, 50, or 100 cub. cents. or grain measures of water, so that the quantities of water employed may be determined by measure.

II. Carbonic acid and sulphuretted hydrogen-gases can only be determined at the well itself by means of the appropriate apparatus.

III. The total weight of the fixed constituents is ascertained by evaporating a measured quantity of the water to dryness, and carefully heating the residue to about 200°. Should the water contain much chloride of magnesium, an error will result from the partial decomposition of that salt, hydrochloric acid and magnesia being produced; this may, however, be avoided by dissolving a weighed quantity of

pure ignited carbonate of soda in the water before evaporating.

IV. The carbonates of protoxide of iron, protoxide of manganese, lime and magnesia, held in solution by free carbonic acid, are precipitated when a large quantity of water is boiled for an hour in a flask. The precipitate is filtered off, dissolved in hydrochloric acid, the sesquioxide of iron precipitated by ammonia, and the protoxide of manganese, lime and magnesia separated as in No. 23.

V. The silicic acid is left undissolved on treating the residue obtained by evaporation, with dilute hydrochloric acid. Should the water contain carbonate of soda, it must be acidulated with hydrochloric acid previously to evaporation. If gypsum be present, a large quantity of water must be employed to redissolve it.

VI. Boracic acid may be detected by mixing the water with carbonate of soda, concentrating by evaporation to a small bulk, and acidifying with hydrochloric acid; if turmeric-paper be dipped in this solution, and dried, it will become brown if boracic acid be present.

VII. The chlorine is precipitated by nitrate of silver after acidifying the water with nitric acid; the precipitate is treated as in No. 1.

VIII. Bromine and iodine, present only in very small quantity, can only be detected and estimated in large quantities of water, or in the mother-liquor. They are recognized as in No. 107. In order to concentrate the bromine, the water may be evaporated to dryness, and all the bromide of sodium, with but little chloride, extracted from the residue by absolute alcohol. When the alcohol has been evaporated or distilled off, the residue is dissolved in water, and a small quantity of nitrate of silver added, with constant

stirring, so that only about $\frac{1}{6}$ of the chlorine may be precipitated as chloride of silver; the precipitate, which contains all the bromine, is weighed, and a certain portion of it analyzed as in No. 107.

IX. The *sulphuric acid* is precipitated by chloride of barium from the water slightly acidified with hydrochloric acid.

X. Potassa and soda. The water is evaporated to about one-half, and mixed, without filtering, with excess of barytawater; the mixture is allowed to cool, and carbonate of ammonia added; in this way, the sulphuric acid, lime, and excess of baryta are precipitated. The filtrate is acidified with hydrochloric acid, evaporated to dryness, and the residue, which is a mixture of chloride of sodium, chloride of potassium and chloride of magnesium, is then cautiously heated nearly to redness. The three metals are separated as in No. 11.

XI. Carbonate of soda. The water is boiled for a long time, the precipitated earthy carbonates filtered off, and the filtrate divided into two equal parts. In one of these, previously acidified slightly with nitric acid, the chlorine is determined by precipitation with nitrate of silver. The other portion is mixed with a slight excess of hydrochloric acid, evaporated to dryness, and the residue heated nearly to redness; it is then dissolved in water and precipitated by nitrate of silver. The difference between this amount of chloride of silver and the former, corresponds to the quantity of carbonate of soda which was contained in the water.

XII. Lime. In the solution filtered from the precipitate obtained in IV, the lime is precipitated by oxalate of ammonia, after addition of chloride of ammonium. See No. 12.

XIII. Magnesia. The solution filtered from the limeprecipitate is concentrated by evaporation, allowed to cool, mixed with concentrated ammonia, and the magnesia precipitated by phosphate of soda. See No. 6.

XIV. Lithia. The lithia is best obtained from the mother-liquor according to the method given in X. The solution filtered from the precipitate is mixed with phosphate of soda, evaporated to dryness, and the residue treated with a very small quantity of water, when phosphate of soda and lithia is left, which should, however, be tested for magnesia.

Or the mother-liquor may be evaporated to dryness with excess of carbonate of soda, the residue extracted with hot water, the filtered solution mixed with phosphate of soda and evaporated to dryness.

XV. Strontia may be sought in the ferruginous and calcareous stalactites and ochreous deposits from waters containing carbonic acid.

XVI. Phosphoric acid. The foregoing remark applies also to the phosphates. Or a large quantity of water may be evaporated to a small bulk, mixed with ammonia, the precipitate filtered off, dissolved in nitric acid, and tested for phosphoric acid with molybdate of ammonia.

XVII. Arsenic acid, in combination with lime or sesquioxide of iron, must likewise be sought, in the stalactites or ochres from such waters, with the aid of Marsh's apparatus. (See Poisoning by Arsenic.)

XVIII. Antimony and copper, to be tested for in the deposit, by sulphuretted hydrogen.

XIX. Fluorine, also contained in the deposit as fluoride of calcium. Or it may be sought in the precipitate obtained by ammonia in XVI, a part of which should be dried and moistened with concentrated sulphuric acid in a platinum 180 soils.

crucible covered with a glass-plate coated with wax and marked in order to test for fluorine. (See No. 81.)

111. SOILS.

The ordinary constituents of soils, which differ much in different soils, and are very variable in quantity, are salts of chlorine, sulphuric acid, phosphoric acid, silicic acid, carbonic acid, nitric acid, with potassa, soda, ammonia, lime, magnesia, alumina, protoxide of manganese and protoxide of iron, together with sand and organic matters consisting of the *débris* of plants, and of the humous substances produced by their decay.

Some of these constituents are soluble in water.

Others are insoluble in water, but soluble in dilute acids, as, for example, the carbonates and phosphates of lime and magnesia.

The remainder are insoluble even in dilute acids; these consist of quartz and of particles of feldspar, mica and hornblende arising from the disintegration of different kinds of rock.

The soil to be examined is collected from different parts of the field, well powdered, allowed to dry in the air, and uniformly mixed.

It is most convenient to determine the greater number of the constituents in separate portions of the soil.

I. Water. A weighed portion of air-dried soil is heated to 100°, and retained at that temperature till its weight is constant. In this way the amount of hygroscopic water is ascertained.

In order to determine the combined water in the salts,

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clay, &c., the soil may be heated to 200° or 300°, when the ammonia also may be expelled.

II. Organic matters. The dry soil is ignited with access of air, moistened with carbonate of ammonia, and again heated nearly to redness. The loss of weight (ammonia and nitric acid being taken into account) indicates the total amount of organic matter.

The amount of nitrogenized organic matter can only be determined by ultimate analysis, when the ammonia and nitric acid must not be neglected in the calculation.

Certain organic substances, such as fatty and resinous matters may be extracted from the dried soil by hot alcohol and ether.

The humous substances may be extracted by boiling the soil with solution of potassa; they are separated, though not completely, from the brown filtered solution, in the form of a brown precipitate, on adding hydrochloric acid.

III. Ammonia. The soil is distilled with solution of soda, and the ammonia collected and determined as in No. 5.

IV. Nitric acid. The analyst must be satisfied with the qualitative detection of nitric acid. The soil is extracted with water, the filtered solution evaporated to a small bulk, mixed with about \(\frac{1}{4} \) its volume of pure concentrated sulphuric acid, and solution of protosulphate of iron added drop by drop; if nitric acid be present, a dark brown, or, if its quantity be very small, a purple-red colour will be produced. Or the very concentrated solution may be heated, in a tube, with copper-filings and concentrated sulphuric acid, when yellowish-red vapours of nitrous acid make their appearance. Or the dry residue may be mixed with anhydrous sulphate of copper and heated in a tube, when yellowish-red vapours are likewise evolved.

- V. The constituents soluble in water. A large quantity of the air-dried soil, from 1000 to 2000 grms, is heated nearly to ebullition, with water, for a considerable time; the residue is filtered off and thoroughly washed with hot water. The whole liquid is evaporated to about its original volume, carefully weighed or measured, and separate portions of it, weighed or measured off, are employed for the determination of the following constituents.
- a. The total weight of the portion soluble in water is ascertained by evaporation to dryness.
- b. Sulphuric acid is precipitated by chloride of barium from the solution acidified with hydrochloric acid.
- c. Chlorine is precipitated by nitrate of silver, after acidification with nitric acid.
- d. Silicic acid. The solution is mixed with hydrochloric acid, evaporated to dryness, the residue extracted with dilute hydrochloric acid, and the silica filtered off.
- e. Lime, magnesia, alumina, protoxide of iron and protoxide of manganese may be contained in the filtrate from d; they may be separated as in No. 74.
- f. Potassa and soda. The solution is mixed with hydrochloric acid, evaporated to dryness, the residue dissolved in a little water, baryta-water added in excess, the mixture digested for some time, filtered off, and the baryta and lime precipitated from the filtrate by carbonate of ammonia. The solution filtered from these can contain only potassa and soda, which are estimated as chlorides, and separated as usual.
- g. Phosphoric acid, which can only be present if the solution contain no lime, &c., is precipitated as phosphate of magnesia-ammonia.
- VI. Constituents insoluble in water, but soluble in dilute hydrochloric acid. From 50 to 100 grms. of the residue

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obtained in V (previously washed, dried and uniformly mixed), are weighed off, mixed with water, in a flask, to a thin paste, heated, and hydrochloric acid gradually added until the effervescence ceases; the mixture is then heated for some time, with frequent agitation, the insoluble residue filtered off and well washed. The solution is concentrated by evaporation, weighed or measured, and divided into separate portions for the different determinations. If the soil contain much organic matter, it must be feebly ignited with access of air previously to the extraction with hydrochloric acid.

- a. Silicic acid. The solution is evaporated to dryness with addition of some nitric acid.
- b. Sulphuric acid. From a weighed portion of the acid solution, filtered from the silica, the sulphuric acid is precipitated by chloride of barium.
- c. Alkalies. Another portion of this solution is treated as in V, f, with baryta-water.
- d. Phosphoric acid, lime, magnesia, alumina, protoxide of manganese, and protoxide of iron are separated and determined in the greater portion of the solution filtered from the silica, according to the method given in No. 24.
- e. The carbonic acid may be determined in a separate portion of the washed soil, as in alkalimetrical examinations.
- f. A small quantity of copper and arsenic sometimes contained in the soil may be determined by a special experiment. See No. 24.

VII. Constituents insoluble in dilute hydrochloric acid. A small quantity (about 5 or 10 grms.) of the residue obtained in VI, is heated with several times its weight of concentrated sulphuric acid, until the greater part of the acid has been expelled. By this treatment especially the

clay is decomposed. The nearly dry residue is digested with dilute hydrochloric acid, the solution filtered off, and analyzed as above, omitting the determination of silicic acid.

The residue left by hydrochloric acid is boiled for a long time with a concentrated solution of carbonate of soda, which dissolves the silica separated by the sulphuric acid. The filtered solution is acidified with hydrochloric acid, evaporated to dryness, and the silica filtered off.

The portion insoluble in carbonate of soda may be a mixture of sand, feldspar, and other minerals not decomposed by sulphuric acid, which may be separated to some extent with the aid of a magnifier. In order to decompose them, they must be treated as in the analysis of feldspar, No. 73.

The greater part of the residue obtained in VI, previously to treatment with sulphuric acid, may be mechanically separated, with tolerable accuracy, into its constituents, by levigation. The residue is stirred up with much water by means of a feather, and the finer suspended portions, consisting chiefly of clay, are repeatedly poured off until only the grains of sand, feldspar, &c., remain behind.

112. ASHES OF PLANTS.*

Salts of KO, NaO, CaO, MgO, Al₂O₃, Fe₂O₃ and MnO, with Cl, F, SO₃, CO₂, and SiO₃

Manganese does not occur in all ashes, and is seldom present in sufficient quantity to determine. Fluorine has

^{*} By Professor Städeler.

been hitherto found only in the stalks of some of the *Graminacea*. Alumina is an essential constituent of the ashes of the *Lycopodiacea*, but is seldom present in appreciable quantity in other ashes. Even iodine, bromine, oxide of copper, and titanic acid have been found, though generally in very minute quantities, in some ashes.

The process of analysis differs according as the ashes do or do not contain more phosphoric acid than is requisite to combine with the sesquioxide of iron, protoxide of manganese, lime, magnesia, and alumina. To the former (containing more phosphoric acid) belong those of seeds, to the latter, those of woods, succulent plants, &c.

I. Ashes of seeds. About 50 grms. of the seeds which have been dried in the air, or at 100°, are thoroughly carbonized by gentle ignition in a platinum crucible; the carbonaceous mass is powdered, moistened with water, and exposed for some time to the air, when the sulphides are converted into sulphates; it is then digested with concentrated acetic acid, water added, the mixture filtered, and the residue washed with hot water till the washings are only slightly acid to test-papers. The carbonized mass is thus entirely, or almost entirely, freed from metallic chlorides; it is introduced, while yet moist, into a platinum crucible, and incinerated as far as possible by a protracted gentle ignition. (At a bright red heat, phosphide of platinum is formed and the crucible corroded.) Finally, a few drops of concentrated nitric acid are added to the ash, which is then ignited in the crucible, the cover of which is placed against its mouth, until the last traces of carbon are burnt off, and a perfectly white ash remains. This ash is added to the saline mass obtained by evaporating the acetic solution; the mixture is gently ignited to decompose the acetates, and weighed.

The ash is dissolved by nitric acid in a carbonic acid apparatus, and the carbonic acid determined from the loss.

The solution is mixed with 10 or 12 volumes of water, and the residue, consisting of undissolved silica (sometimes also of sand) and charcoal, is collected upon a filter (previously dried at 100°, weighed, carefully removed from the filter, and digested with very dilute solution of soda, which readily dissolves all the silica, except that present in the form of sand; the residue of sand and charcoal is collected upon the filter previously employed; its weight, after being dried at 100°, is deducted from the total weight of the ash. The weight of the silicic acid is determined from the loss.

From the filtered solution containing the saline constituents, the chlorine is precipitated by nitrate of silver, an excess of the precipitate removed by hydrochloric acid, the sulphuric acid precipitated by chloride of barium, and the excess of baryta separated by careful addition of sulphuric acid.

The filtrate is evaporated to dryness, the residue treated with concentrated hydrochloric acid, and digested with it for some time, in order completely to expel the nitric acid, and to convert any pyrophosphoric acid into the tribasic form. The hydrochloric acid is expelled as far as possible, a sufficient quantity of water afterwards added, and the solution filtered from the undissolved silica, which is ignited, weighed, and calculated together with that previously obtained.

From the solution, the iron, manganese, alumina, lime, and magnesia, are precipitated by ammonia as phosphates, which are collected, after six or eight hours, upon a filter, ignited and weighed. The precipitate is dissolved by

digestion with concentrated hydrochloric acid, the free acid nearly neutralized with soda, and the solution mixed with acetate of soda, when the phosphates of sesquioxide of iron and alumina are precipitated. These are ignited and weighed, and if necessary (unless the ignited precipitate has a pure brown colour), separated according to No. 19.— From the filtrate, the lime is precipitated by oxalate of ammonia, and the magnesia, as phosphate of magnesia-ammonia, by merely adding an excess of ammonia; the phosphoric acid previously in combination with lime is calculated from the loss.—If manganese be present, it is precipitated together with the phosphate of magnesia-ammonia, to which it imparts a grey or black colour after ignition. The separation is effected as in No. 24.

The solution from which the phosphates have been precipitated by ammonia, now contains only the alkalies and the remainder of the phosphoric acid. The latter is precipitated (together with sulphuric acid) by chloride of barium, and the excess of baryta removed by sulphuric acid or by neutral carbonate of ammonia; the filtrate is evaporated to dryness, the residue ignited, and the alkalies weighed as chlorides or sulphates. For their separation, see No. 4.—The precipitate produced by chloride of barium is exhausted with nitric acid, sulphuric acid added to effect the complete separation of the baryta, and the phosphoric acid precipitated from the filtrate, previously mixed with an excess of ammonia, as phosphate of magnesia-ammonia.

II. Ashes of wood, vegetables, &c. Of those vegetables which yield a large amount of ash, 50 grms. may be taken for examination; but of the different kinds of wood, which are usually poorer in mineral constituents, and of the Graminacea, the ash of which contains much silica, about 100 grms. should be employed. The substances are car-

bonized in a platinum crucible, and the mass thrown immediately into a flat porcelain dish, where it generally smoulders for a long time, and is, for the most part, converted into ash. The incineration is completed in the platinum crucible.

The analysis of these ashes only differs from that of the preceding in that these contain a larger quantity of the alkaline earths than is necessary to combine with the phosphoric acid, so that the total amount of that acid is separated upon adding ammonia. The precipitate is immediately filtered off, and the filtrate mixed, first with sulphide of ammonium, to precipitate the manganese, then with oxalic acid for the lime, and lastly with phosphate of ammonia to separate the magnesia. Any excess of phosphoric acid may be separated, as directed above, from the alkalies, which are then weighed as chlorides or sulphates.

The stalks of the *Graminaceæ* usually leave an ash which cannot be completely decomposed by nitric or hydrochloric acid. The weighed silicate remaining undissolved, is decomposed most conveniently with hydrofluoric acid, and the bases, previously in combination with silicic acid, may then be estimated in the solution. The silicic acid is determined from the loss. In this case, the determination of the charcoal and sand must, of course, be omitted.

113. GUANO.

Guano consists of the partially decomposed excrement of sea-birds. It contains a great many substances, some soluble, others insoluble in water. The constituents upon which depend its important action and application as a manure, are: organic, chiefly nitrogenized matters; salts of ammonia; phosphates, especially phosphate of lime; and salts of the alkalies. The amount of these constituents indicates the value of the guano. It is important to test this manure, since different specimens consist not only of various kinds of genuine guano of different degrees of richness, but samples also come into the market which are adulterated with common earth, loam, lime, sand, pebbles, and crude common salt or Glauber's-salt.

Genuine guano presents the appearance of a moist yellowish-brown earth, mixed here and there with white fragments or lumps. Very few and rare specimens are white. It has a peculiar excrementitious or urinous odour, and a feeble penetrating saline taste.

It is chemically tested in the following manner:

I. The guano is mixed, in a dish, with hydrate of lime (slaked lime stirred with water to a thin cream), when it should emit, especially when heated, a powerful odour of ammonia. In order to compare different specimens, the same quantity, say ½ oz. of each, is taken. Since the value depends partly upon the amount of ammonia present, the better sorts of guano will evolve the stronger odour of that gas.

II. Two ounces (or from 50 to 60 grms.) of guano, finely powdered and uniformly mixed, are weighed in a counterpoised porcelain capsule, and heated on a water-bath until it is perfectly dry and suffers no farther diminution of weight. The loss of weight expresses the amount of moisture contained in the guano. Good guano loses only between 8 and 15 per cent of water, but if fraudulently moistened, it may lose 20 per cent, or even more.

III. Half an ounce (or from 15 to 20 grms.) of guano is

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weighed, and heated over a large spirit-lamp, or gas-burner, in a porcelain or platinum crucible, with free access of air, until all organic matter has burnt off, and the guano is converted into a white or greyish ash. Good guano, when treated in this way, leaves from 30 to 35 per cent of ash, while bad guano leaves from 60 to 80 per cent, and that which has been fraudulently adulterated leaves still more. The ash of genuine guano, whether of good or bad quality, is always white or greyish; a yellow or reddish colour bespeaks an admixture of clay or earth. Good guano, when first heated, evolves white vapours, with a powerful odour of ammonia.

IV. A similar quantity of guano is mixed, in a dish, with several times its volume of water; heat is then applied, and the mass thrown upon a small filter (previously dried in the water-bath and weighed); the residue on the filter is washed with hot water till a small portion of the washing-water is not rendered turbid by adding chloride of calcium and ammonia. The filter, with the washed guano, is then thoroughly dried in a water-bath, and weighed. The better the quality of the specimen, the less insoluble residue will be obtained. Good samples of guano leave from 40 to 45 per cent, those of bad quality as much as 70 or 80. If the guano be adulterated with common salt or with Glauber's-salt, it will behave, to this test, like a genuine specimen, but will furnish a greater quantity of ash in Experiment III.

V. The guano under examination, may be treated with moderately strong hydrochloric acid. Good guano effervesces but slightly; a specimen of guano, adulterated with chalk, would effervesce strongly, and would leave a proportionally larger quantity of ash in Experiment III.

VI. The ash obtained in III, is dissolved in dilute

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hydrochloric acid, which should give rise only to slight effervescence, if the guano be unadulterated. The solution is filtered from the residue, the latter washed, dried, thoroughly burnt, together with the filter, in a weighed crucible, over the spirit-lamp, and weighed. This insoluble residue, consisting partly of sand, amounts, in good (undried) guano, to only 1 or 2 per cent.

VII. The filtered hydrochloric solution is mixed with a slight excess of ammonia. The precipitate thus produced consists almost entirely of phosphate of lime. It is filtered off, washed, dried, and ignited; its quantity in good

guano amounts to 20 or 25 per cent.

VIII. The filtrate from this precipitate should furnish only slight indications of lime on addition of oxalic acid; but if the guano be adulterated with chalk, this reagent will produce a very considerable precipitate. This solution ought therefore to contain only the alkaline salts, amounting to 5 or 10 per cent of the original undried guano. In order to determine them directly, which is generally unnecessary for practical purposes, the solution must be mixed with some more chloride of ammonium, and evaporated to dryness; the residue is heated to volatilize the excess of chloride of ammonium, and to convert the sulphates into chlorides, weighed, and farther treated as in No. 4.

IX. The aqueous solution, which was obtained in the lixiviation-test (IV), and of which a fresh quantity may be prepared so as to be saturated, has a brown colour and a saline taste. When evaporated it evolves ammonia, emits an urinous odour, and leaves a brown crystalline mass, consisting chiefly of sulphates of potassa and soda, chloride of ammonium, oxalate and phosphate of ammonia. This solution exhibits the following reactions:

When mixed with hydrate of potassa, it smells strongly of ammonia.

With chloride of ammonium, ammonia, and sulphate of magnesia, it gives an abundant pulverulent precipitate of phosphate of magnesia-ammonia.

When acidified with acetic acid and tested with chloride of calcium, it gives a copious precipitate of oxalate of lime.

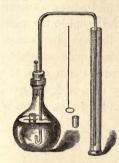
After addition of excess of hydrochloric acid, it gives, with chloride of barium, a considerable precipitate of sulphate of baryta.

X. When guano is exhausted with cold water, and the residue digested with a weak solution of caustic soda, uric acid is extracted. The solution is filtered, and feebly acidulated with hydrochloric acid, when the uric acid is precipitated. After being filtered off and washed, it is easily soluble in caustic potassa, and may be reprecipitated by hydrochloric acid. If it be dissolved in warm dilute nitric acid, the solution evaporated to dryness, and the residue moistened with carbonate of ammonia, a fine purple-red colour is produced.

XI. The quantity of organic matter can be estimated directly only by an ultimate organic analysis. In good undried guano it amounts, taking the ammonia into account, to about 50 per cent.

XII. The exact determination of the nitrogen requires also an ultimate analysis. This element should amount to 12 or 14 per cent; bad samples contain only from 1 to 6 per cent. The quantity of nitrogen may, however, be approximatively determined by the following method, which therefore allows us to ascertain rapidly the value of different specimens of guano. It depends upon the circumstance that when guano is treated with a solution of chloride of

lime (hypochlorite of lime), the nitrogen of the organic matter and of the ammoniacal salts is evolved as gas.* Instead of collecting and measuring the gas evolved, which would be scarcely practicable, on account of the violent effervescence, the volume of water which is expelled by the



gas is ascertained by means of the simple apparatus represented in the figure; it consists of a flask capable of containing about ½ pint, provided with a narrow gas-delivery-tube bent twice at right angles. One limb, rather the shorter of the two, is passed, air-tight, through the cork of the flask, and bent upwards to prevent, as far as pos-

sible, the escape of bubbles of gas. This tube descends nearly to the bottom of the flask. A second very narrow short tube is also passed through the cork, and serves for the escape of air when the cork is introduced. The longer limb of the delivery-tube dips into a tall cylinder or tube, which is graduated to cubic centimeters, or cubic inches. The flask is half-filled with solution of chloride of lime;† 1 grm. of guano is then weighed in the small glass vessel (the end of a test-tube) in which a few small shot have been placed, in order that it may float upright. With the aid of the handle of iron-wire shown in the figure, the tube is let down so as to float upon the surface of the

^{*} Farther experiments are required to show that all the nitrogen is here evolved in the gaseous state, and to ascertain how the various nitrogen-compounds behave with chloride of lime.

[†] This solution must be carefully prepared and kept in a dark place, in a closed vessel. It must contain an excess of hydrate of lime, and therefore need not be perfectly clear.

solution of chloride of lime; the cork with the tube is then tightly adjusted, the orifice of the smaller tube closed with wax, and the flask shaken so that the little vessel may fill and sink. A volume of liquid equal to that of the nitrogen evolved from the guano then flows into the graduated cylinder; when no more liquid passes over, the cylinder is depressed so as to bring the liquid to the same level as that in the generating-flask; the wax plug is then removed, the cork withdrawn, and the liquid still contained in the delivery-tube is allowed to run into the cylinder, where the whole is carefully measured. 1 grm. of good guano evolves between 70 and 80 cub. cents. of gas.

114. OXALATE AND PHOSPHATE OF LIME.

A mixture of these two salts dissolves in nitric acid without effervescence, and is reprecipitated from the solution by ammonia. If it be digested, when freshly precipitated, with acetic acid, the phosphate of lime may be dissolved, while the oxalate is left.

If the mixture be previously ignited, it dissolves in nitric acid with effervescence, and ammonia then precipitates from the solution only the phosphate of lime, while the lime which had been in combination with oxalic acid remains in solution, and may be precipitated by oxalate of ammonia, and quantitatively determined. Phosphate of lime, when freshly precipitated, may be recognized by the yellow colour which it assumes when moistened, on the filter, with nitrate of silver. It is analyzed as in No. 13.

If the two salts be dissolved in the smallest possible quantity of hydrochloric acid, and the solution mixed with

an excess of acetate of soda, the oxalate of lime is precipitated, while the phosphate remains in solution; from the latter, the lime may be precipitated by oxalate of ammonia, and afterwards the phosphoric acid by sulphate of magnesia and ammonia, as in No. 9.

When the mixture of the two salts is treated with concentrated sulphuric acid, oxalic acid is converted into carbonic acid and carbonic oxide, so that by employing the apparatus described in the article upon alkalimetry, its amount may be inferred from the loss of weight.

By gently heating the mixture with an excess of finely-powdered binoxide of manganese or neutral chromate of potassa, or with binoxide of lead and dilute sulphuric acid, all the oxalic acid is converted into carbonic acid, the quantity of which may be determined by the use of the apparatus above alluded to. 2 equivs. of carbonic acid correspond to 1 equiv. of oxalic acid.

If binoxide of lead be employed in this operation, the quantitative determination of the phosphoric acid may be effected at the same time; for this purpose, the mixture is digested for some time, to liberate the whole of the phosphoric acid; several volumes of alcohol are then added, in order to separate the sulphate of lime, the solution filtered, and the residue washed with alcohol. From the filtrate, after the evaporation of the alcohol, the phosphoric acid may be precipitated by sulphate of magnesia and ammonia.

A very accurate method of estimating oxalic acid consists in converting it into carbonic acid by means of a solution of terchloride of gold, weighing the reduced gold, and calculating thence the amount of oxalic acid; 3 equivs. of the latter reduce 1 equiv. of gold=197.

For this purpose the mixture of the two salts is dissolved

in the smallest possible quantity of hydrochloric acid (a large excess impedes the reduction of the gold), mixed with an excess of a solution of terchloride of gold, or better, of sodio-chloride of gold, diluted with much water, and heated to ebullition. The reduced coherent gold is easily washed; it is to be dried, ignited, and weighed.

The excess of gold is removed from the solution by sulphuretted hydrogen, or by boiling with oxalic acid, and the phosphoric acid and lime are then separated and estimated as in No. 13.

115. ALKALIMETRY.

The specimens of potashes and soda-ashes met with in commerce contain very variable quantities of foreign substances. The amount of carbonated alkali, upon which their value alone depends, varies between 40 and 95 per cent.

The potashes contain chiefly chloride of potassium, sulphate, silicate, and phosphate of potassa, and carbonate, phosphate, and silicate of lime.

The soda generally contains chloride and sulphide of sodium, sulphate, silicate and hyposulphite of soda, and often also hydrate of soda.

The amount of alkaline carbonate present in the sample, may be determined by several methods.

I. By the standard solution test, i. e., by exactly neutralizing a weighed portion with dilute sulphuric acid of known strength.

In order to prepare the test-acid, a known quantity, say 70 grms., of concentrated sulphuric acid, are diluted with 600 grms. of water.

5 grms. of pure anhydrous carbonate of soda are weighed, dissolved in *hot* water, and the solution coloured blue with a little tincture of litmus.

The test-acid is then added to the solution, from a burette, very carefully as the point of neutralization is approached, until the colour is just changed to red, and streaks which are made with the liquid upon litmus-paper, remain red after drying.

The number of measures of acid employed is then observed, and the whole of the test-acid is diluted with so much water, that exactly 100 measures are required to neutralize 5 grms. of pure carbonate of soda. This stock of test-acid is preserved in a well-stopped bottle. It indicates immediately the percentage of caustic or carbonated alkali in a specimen of potashes or soda, provided that a quantity of the sample be employed, which is equivalent to 5 grms. of carbonate of soda.

100 measures of test-acid saturate 5.000 grms. of carb. of soda,

100 ,, ,, ,, 2.935 ,, of soda,

100 ,, ,, 6·487 ,, of carb. of potassa, 100 ,, ,, 4·421 ,, of potassa.

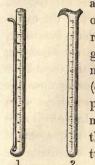
So that if 6.487 grms. of a sample of potashes be taken, the number of measures of acid employed will express, directly, the percentage of carbonate of potassa, or if 4.421 grms. be used, of anhydrous potassa, contained in the specimen.

Instead of sulphuric acid, pure crystallized oxalic acid may be very conveniently employed for preparing the test-solution. An equivalent of the acid (63 grms.) is introduced into a flask of 1 litre capacity, which is then two-thirds filled with water; the acid is allowed to dissolve, and so much water added that the whole solution may measure 1 litre or 1000 cubic centimeters, at 17.5° C.

One hundred cub. cents. of this test-acid then will exactly neutralize 10 of an equivalent proportion of either alkali. It is therefore necessary to weigh out $\frac{1}{10}$ of an equivalent proportion (in grammes) of the anhydrous alkali to be tested, that is, 6.92 grms. of potashes, or 5.32 grms. of soda-ash. In order to obtain perfectly accurate results, the process is conducted as follows: The solution of alkali to be tested, is introduced into a flask, coloured with tincture of litmus, and the test-acid poured into it from a burette, until the colour changes from blue to violet, and the effervescence is very feeble. The solution is now heated to ebullition, and more acid added until the colour has become decidedly red. 5 or 10 cub. cents. of the test-acid are then added in excess; the alkali will be now supersaturated. By boiling, agitating, and finally sucking out with a glass tube, the last traces of carbonic acid are removed. It is now required to determine exactly how far the neutralization of the alkali has been exceeded; for this purpose a standard solution of caustic soda is employed, of such strength that it is exactly neutralized by an equal volume of the test-acid; * this solution is added from a burette graduated to 10 cub. cent., when the red colour rapidly changes to violet, and then suddenly to pure blue. The number of cubic centimeters of sodasolution employed, is then deducted from the volume of test-acid previously added; the remainder gives the percentage of pure alkaline carbonate.

The dropping-tubes or burettes employed for these

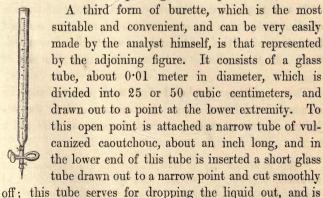
^{*} This solution of soda must be perfectly free from carbonic acid. In order to preserve it in that state, the bottle is closed with a cork, through which passes an ordinary chloride-of-calcium-tube, open at both ends, and filled with a mixture of Glauber's-salt and quick-lime in powder.



analyses with standard solutions, are made of different forms. The commonest is that represented in Fig. 1, and consists of a glass tube, closed at one end, about 0.25 meter (or 12 inches) long, and 0.01 meter (or ½ inch) in diameter; into the lower part of this tube is cemented another, very much narrower, which is fixed parallel with the larger tube; the extremity of the small tube is bent outwards and sharply cut off, so that the liquid may be conveniently

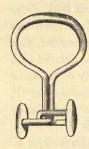
poured from it. The whole of the vessel is divided into known volumes, and it is preferable to take from 25 to 50 cub. cents., and to divide these into fractional parts. The zero should be placed at the top of the scale, below the level of the orifice of the spout.

Another form is that shown in Fig. 2, which consists of a single divided tube furnished at the top with a spout, and with an orifice for pouring in the liquid.



tightly connected with the graduated tube in such a

manner that a considerable interval may be left between the ends of the two tubes. Upon this part of the caoutchouc tube is fixed a clamp made of thick brass-wire, shown with its actual dimensions, in the accompanying



figure, so constructed that the caoutchouc tube may be opened by pressing upon the two ends of the clamp, and closed when the pressure is removed. In order to use this tube, it is fixed in a stand, in a vertical position, above the vessel containing the liquid to be tested. By pressing upon the ends of the little clamp, the caoutchouc tube is opened, and the liquid allowed to

flow out, even in single drops, if required.* At the commencement of the operation, the tube is filled with the test-liquid, a portion of which is then made to flow out, by pressing upon the clamp until it stands exactly at the zero of the scale.

II. By determining the carbonic acid evolved.

The carbonic acid is liberated from a weighed portion of the alkali, in an apparatus which is previously weighed (together with the acid used to effect the decomposition), and the carbonic acid determined from the loss of weight.

The apparatus employed for this purpose may be arranged in different ways. That represented in the adjoining figure, of about $\frac{1}{3}$ its real dimensions, will render

^{*} This apparatus may be obtained through the kindness of its inventor, Dr. Mohr, of Coblenz. It is not applicable, however, to the testing with permanganate of potassa (No. 101), since that salt is decomposed by the caoutchouc.



apparent the general principle, upon which they are constructed, and will itself fully answer the purpose. It consists of a small light flask, closed by a cork perforated with two holes, in one of which is inserted a tube filled with fragments of chloride of calcium, and in the other, a narrow glass tube, running nearly parallel with the inner wall of the flask, and reaching almost to the

surface of the liquid; above the cork, this tube is bent at right angles.

The specimen to be examined is weighed in the flask, the latter about one-third filled with water, and the small tube full of acid introduced with a pair of pincers; this tube must be of such a length that it cannot fall down in the flask, but may assume the position indicated in the figure. Sulphuric acid is to be preferred for effecting the decomposition of the carbonate, and should be employed in quantity more than sufficient to expel the whole of the carbonic acid. (For the carbonates of lime, baryta and lead, nitric acid must be employed.)—The cork, with the chloride-of-calcium-tube, and the bent tube is then introduced, air-tight, into the neck of the flask, the whole apparatus accurately weighed, and the orifice of the bent tube perfectly closed with a small cork or with wax.

The flask is then carefully inclined so that a small quantity of the acid may run out of the tube and decompose the carbonate. The carbonic acid which is evolved escapes through the chloride-of-calcium-tube, in which any water which may have been carried off with it is retained. No fresh acid is allowed to flow out of the tube until the

effervescence caused by the first portion has ceased, and does not recommence upon gentle agitation. When, at length, the effervescence has entirely ceased, so that the salt is completely decomposed, the plug is removed from the small tube and suction applied, by the mouth, to the tube containing chloride of calcium, until the air passing through the flask no longer tastes of carbonic acid. In very exact experiments, a second chloride-of-calcium-tube must be attached to the small bent tube, to retain the moisture of the air.

1. Potashes.—The amount of water is ascertained by heating the specimen, for some time, to about 200°. For this purpose from 2 to 5 grms. of potashes may be taken.

In order to determine immediately, without calculation, the percentage of potassa in carbonate of potassa, by means of the above apparatus, 3·14 grms. of the specimen must be taken. Since 3·14 grms. of pure carbonate of potassa evolve 1·00 grm. of carbonic acid, the number of centigrammes of carbonic acid evolved will represent the percentage of carbonate of potassa.

2. Soda.—2·41 grms. of soda are employed. This is the quantity of *pure* carbonate of soda which evolves 1·00 grm. of carbonic acid.

Should caustic soda be contained in the specimen, which may be known by the alkaline reaction of the solution after adding an excess of chloride of barium, the following modification of the process is necessary:

2.41 grms. of the anhydrous sample are mixed with about 3 parts of pure quartz-sand, and about \(\frac{1}{3} \) part of powdered carbonate of ammonia; the mixture is moistened with water, and, after some time, gently heated till

all water and ammonia are expelled. The dry residue is then treated, as usual, in the above apparatus.

In order to prevent any inaccuracy arising from the presence of sulphide of sodium or hyposulphite of soda in the specimen, a solution of chromate of potassa is added previously to the evolution of carbonic acid, in order to oxidize these impurities.

116. VALUATION OF MANGANESE-ORES.

Good manganese-ore, which consists almost entirely of binoxide of manganese, is crystalline, yields a black powder, and, after being dried at a gentle heat, gives no water, or only traces, when heated to redness. Manganese-ore, however, generally contains foreign minerals, especially the hydrated sesquioxide of manganese. In order to determine the amount of binoxide, or, in other words, of available oxygen, several methods may be employed.

I. A weighed quantity of the manganese-ore, powdered as finely as possible, is introduced into the apparatus employed for the quantitative estimation of carbonic acid, where it is brought in contact with sulphuric acid and a solution of oxalic acid, when sulphate of protoxide of manganese is produced, since all the available oxygen, which may be regarded as in combination with the protoxide of manganese, is evolved in the form of carbonic acid.

One equiv. of pure binoxide of manganese = 43.6, yields 2 equivs. = 44 of carbonic acid. So that 0.99 grm. of binoxide of manganese evolves 1.00 grm. of carbonic acid. It is best to employ three times that quantity of the manganese-ore, viz.: 2.97 grms., which are mixed with a solution of 2.5 grms. of neutral oxalate of potassa;

the sulphuric acid is allowed to flow into this mixture, and the amount of carbonic acid evolved is divided by 3. The quotient expresses the percentage of binoxide of manganese contained in the ore.

II. The finely-divided manganese-ore is weighed, and mixed with water, in a flask capable of being tightly closed; several bright strips of copper, previously weighed, are then introduced, and a quantity of hydrochloric acid added. The flask is then closed with a cork and narrow tube, and the contents digested until all the manganese has dissolved, care being taken that no chlorine is evolved. The liquid is then heated to ebullition for a quarter of an hour, the flask closed air-tight, and allowed to cool; the solution is poured off, the residual copper washed, first with very dilute hydrochloric acid, then with pure water, dried, and weighed. 2 equivs. of copper = 63.4 parts require for their conversion into subchloride, 1 equiv. = 71 parts of chlorine.

Then 63.4:71 as the amount of copper dissolved is to x (the amount of chlorine sought.)

1.22 grms. of pure binoxide of manganese evolve 1.00 grm. of chlorine, and therefore are capable of effecting the solution of 1.78 grms. of copper.

117. CHLORIMETRY.

The "lime-bleach" of commerce is a variable mixture of hypochlorite of lime and chloride of calcium, with hydrate of lime. When treated with an acid, it evolves the whole of the chlorine in a free state. In order to determine its value, i. e., the amount of available chlorine which it contains, different methods are employed.

I. Fourteen grms. of pure arsenious acid are dissolved in solution of potassa, and so much water added that the liquid may occupy 2000 divisions of the graduated burette. 100 measures, therefore, of this solution contain 0.7 grm. of arsenious acid, and the solution of chlorine which is required to convert this into arsenic acid, contains 0.5 grm. of chlorine, since 1 equiv.=99 of arsenious acid, requires, for its conversion into arsenic acid, 2 equivs.=71 of chlorine.

Five grms. of chloride of lime are weighed off, intimately mixed with water, by trituration, rinsed into a cylindrical glass, and so much water added that the whole may occupy 200 measures of the burette.

One hundred measures of the arsenic-solution are then introduced into a beaker, diluted with water, an excess of hydrochloric acid added, and the liquid coloured with one or two drops of sulphindigotic acid.

The solution of chloride of lime is well mixed by agitation, introduced into the burette, and added to the coloured arsenic-solution until the colour just disappears. The solution of chloride of lime required to produce this effect contains 0.5 grm. of chlorine.

For example, if 90 measures of the solution of chloride of lime had been employed, the 5 grms. of chloride of lime would have contained 1.111 grms. of chlorine, or 22.22 per cent.

Perfectly pure chloride of lime (Ca Cl+CaO, ClO), which is never met with in commerce, contains 48.9 per cent of available chlorine.

II. A weighed quantity of chloride of lime is mixed with water, in a flask, an excess of protochloride of iron, free from sesquichloride, added, and afterwards some hydrochloric acid. Several bright weighed strips of copper are

then introduced, and the solution boiled until the protochloride at first formed is converted into subchloride; the copper is then withdrawn, washed, dried, and weighed. The calculation is effected as in No. 116.

118. ANALYSIS OF NITRE.

In order to determine the amount of moisture in crude nitre, from 5 to 10 grms. of the specimen, previously reduced to powder and dried by exposure to air, are heated to about 150°.

The determination of the quantities of the foreign salts present in the specimen, such as sulphates and chlorides, lime and magnesia, by the ordinary methods, would occupy too much time; it would be preferable to estimate them by means of standard solutions of the reagents, *i. e.*, by measuring the quantities of the latter required to effect complete precipitation.

The appearance of the fracture is regarded as an indication of the quality of the nitre; in pure nitre, the fracture is lustrous, and exhibits a well-defined crystalline appearance; but if not more than 2 per cent of common salt be present, it is granular and dull. An admixture of nitrate of soda (Chili saltpetre) has the same effect.

Another method, which is likewise, however, inaccurate, but is most readily applied in practice, depends upon the circumstance that a solution of pure nitre, at the temperature at which it is saturated, is still capable of dissolving other salts, especially chloride of sodium. 400 grms. of the powdered specimen are shaken with 500 cub. cents. of a solution of pure nitre; the salt is then filtered off, again washed with 250 cub. cents. of a saturated solution of nitre, dried at 100°, and weighed.

The loss of weight expresses the amount of the foreign salts. Since this process is liable to error from many causes, and gives the amount of pure nitre, on an average, 2 per cent too high, these 2 per cent must not be neglected in calculating the amount of impurity present.

The following process is more accurate, which consists in converting the nitre contained in any specimen into carbonate of potassa, the amount of which is then determined by means of the standard acid, as in testing potashes.

9.475 grms. of pure nitre furnish a quantity of carbonate potassa, which is capable of saturating 100 measures of the acid mentioned in the testing of potashes; so that if this amount of impure nitre be employed, the number of measures of acid indicate at once the percentage of pure nitrate of potassa in the specimen.

One-fourth of the above quantity (2.369 grms.) of the crude nitre is weighed out, intimately mixed with 1 grm. of ignited lamp-black, and with 12 grms. of ignited and finely-powdered common salt, which serves to moderate the violence of the combustion. The mixture is introduced into a platinum crucible, and heated to redness over a large spirit-lamp or gas-burner. When cool, it is dissolved in water, and the standard acid added in the manner directed for testing samples of potashes. The number of measures of acid employed is multiplied by 4, in order to obtain the percentage of pure nitre in the specimen.

In following this method it is impossible to determine

In following this method it is impossible to determine the weight of the expelled carbonic acid by means of the apparatus generally employed for this purpose, on account of the large quantity of common salt which has been added.

119. GUNPOWDER.

I. For the estimation of moisture, 5 or 6 grms. of powder are dried over sulphuric acid, or in the air-bath at 100°.

II. A similar quantity of powder is moistened with water, triturated in a mortar, rinsed into a filter, and thoroughly washed. The solution of nitre thus obtained is evaporated to dryness in a small weighed porcelain dish, the dry residue heated for some time to 200°, or even till the nitre fuses, and its weight determined.

III. In order to determine the sulphur, 5 grms. of powder are intimately mixed with 5 grms. of anhydrous carbonate of soda, 5 grms. of nitre, and 20 grms. of decrepitated chloride of sodium, and the mixture heated to redness in a platinum crucible. When cool, the mass is dissolved in water, the solution slightly acidified with nitric acid, and the sulphuric acid precipitated by chloride of barium. (See No. 3.)

The amount of carbon may be inferred by difference. In order to determine its quality, and to ascertain whether it has been completely or incompletely carbonized, the mixture of sulphur and carbon is boiled with a solution of protosulphide of potassium, which dissolves the sulphur, leaving the carbon which must be well washed and dried. The sulphide of potassium should not contain any free potassa, since this might dissolve an imperfectly carbonized charcoal.—Bisulphide of carbon may also be employed for the extraction of the sulphur.

120. HYDROCYANIC ACID.

In order to determine the strength of a solution of pure hydrocyanic acid, a weighed quantity of it is treated with solution of nitrate of silver, which is added gradually, and with frequent agitation, until no farther precipitation takes place, and the odour of hydrocyanic acid has entirely disappeared.

The precipitated cyanide of silver is collected upon a filter (previously dried at 120° and weighed), washed, dried at 120°, and its weight determined.

For the estimation of the amount of hydrocyanic acid in the aqua amygdalarum amararum and aqua laurocerasi, they must first be mixed with ammonia, then with nitrate of silver, and lastly with nitric acid.

If hydrochloric acid be contained in the solution together with hydrocyanic acid, they are both precipitated from a weighed portion of the solution by nitrate of silver, and the precipitate weighed upon a filter dried at 120°. Another weighed portion of the solution is mixed with solution of borax and evaporated to perfect dryness. In this way, all the hydrocyanic acid is volatilized, and the hydrochloric acid converted into chloride of sodium. The dry residue is dissolved in water, the solution acidulated with nitric acid, and the chlorine precipitated by nitrate of silver.

Another method, which may be executed with great rapidity, and suffices for the determination of the hydrocyanic acid in any solution, whether bitter almond-water or laurel-water, &c., or for ascertaining the quantity of cyanogen in crude cyanide of potassium, depends upon the circumstance that 1 equiv. of cyanide of potassium forms, with 1 equiv.

of cyanide of silver, a soluble compound which is not decomposed by an excess of alkali, but from which nitrate of silver precipitates the cyanide, or if a little solution of chloride of sodium be previously added, the chloride of silver. The weighed solution, containing hydrocyanic acid is mixed with solution of potassa till it has a strongly alkaline reaction, and a standard solution of silver is then added till a permanent precipitate begins to appear. 1 equiv. of silver employed in the standard solution corresponds exactly to 2 equivs. of hydrocyanic acid.

Ten grms. of pure silver are dissolved in nitric acid, the solution evaporated to perfect dryness, and diluted with so much water, that the whole solution may occupy 1000 cub. cents. 100 cub. cents. of this solution, which contain therefore 1 grm. of silver, represent 0.5 grm. of anhydrous hydrocyanic acid, or 0.481 cyanogen, or 1.206 of cyanide of potassium.

121. FERROCYANIDE OF POTASSIUM. 2 K Cy + Fe Cy + 3 HO= K_2 Cfy + 3 HO.

The water is determined by heating the finely-powdered salt for some time to about 200°.

The cyanogen can be directly determined only by an organic analysis, i. e., by a combustion.

For the determination of the amount of iron, the salt is intimately mixed with $1\frac{1}{2}$ parts of nitre, and as much carbonate of soda, and the mixture gradually heated to redness in a platinum crucible. On dissolving the fused mass in water, the iron remains behind in the form of sesquioxide, which is washed, ignited, and weighed.

Since it is liable to contain a small amount of alkali, it should be dissolved in hydrochloric acid, reprecipitated by ammonia, washed and ignited.

In order to determine the potassium and iron, the salt is dissolved in water, and the solution precipitated by acetate of lead. The precipitate of ferrocyanide of lead is filtered off and washed.

From the solution, which contains all the potassium as acetate of potassa, the excess of lead is precipitated by sulphuretted hydrogen or sulphide of ammonium, the filtered solution evaporated, the residue ignited, the carbonate of potassa converted, by hydrochloric acid, into chloride of potassium, and weighed in that form, after gentle ignition. The ferrocyanide of lead is decomposed by digestion with sulphide of ammonium, the solution of ferrocyanide of ammonium filtered off, evaporated, and the residual mass ignited, with access of air, until only pure sesquioxide of iron is left.

Ferrocyanide of potassium may probably also be decomposed by heating with bisulphate of ammonia. The residue after ignition would then consist of a mixture of sesquioxide of iron and sulphate of potassa, from which the latter might be extracted with water. Or, to ensure an accurate result, the ignited residue might be dissolved in hydrochloric acid, the sesquioxide of iron precipitated by ammonia, the solution evaporated, and the residual sulphate of potassa ignited and weighed.

122. EXAMINATION FOR ARSENIC IN CASES OF POISONING.

When poisoning by arsenic is suspected, the poison must be sought in the contents of the stomach and in-

testines, in the substance of these organs even, and in other entire organs, as the liver, spleen, and lungs; an examination must also be made of the vomited matters, and of the surrounding objects, upon which these may have fallen; the urine and fæces should also be tested for arsenic. The nature of the case will decide in which particular direction the arsenic is to be looked for. It may also sometimes be necessary to examine the remaining portions of suspected food, or the vessels in which the food has been contained, or even the vessel or paper which may have been used to contain the arsenic. When the body has been long interred, and is far advanced in putrefaction, and the wood of the coffin has rotted away, it becomes necessary to test the surrounding earth for arsenic which may have been derived from the body.

The chemical investigation must be preceded by a very careful examination of the contents of the stomach and intestines, or of the vomited matters. The substances to be examined are spread out in new and clean porcelain dishes, turned over with perfectly clean glass rods or spatulas, and examined with the help of a lens. The analyst should seek especially for small white hard particles or grains of undissolved arsenious acid, which may be carefully picked out with a pair of pincers. These must be looked for especially in the folds of the mucous coat of the stomach and intestines. By stirring up the contents with distilled water, or better, with spirit, and pouring off the lighter organic matters, it is often possible to separate a considerable quantity of the heavy arsenic-powder.

In a judicial investigation of this description, the aim of all chemical operations is to obtain the arsenic in its elementary solid state, as the so-called *metallic arsenic*.

In this form alone it is possessed of such highly characteristic properties as to render it impossible to confound it with any other substance, and to allow it to be distinctly recognized even when in almost imponderable quantities. Moreover, all evidence of its presence is insufficient, unless it can be laid before the tribunal in this form; and all other forms and states of combination must be considered as affording inconclusive testimony as to the existence of arsenic in the substance under examination. This preparation or isolation of arsenic in its metallic state, even in the smallest, almost imponderable quantities, is very simple and easy. Great difficulties, however, present themselves, when it is necessary to extract these traces of arsenic, which are diffused through a whole body, from the great mass of organic matter, and to convert them into some form of combination, from which the arsenic can be extracted in the metallic state.

It is most convenient, in considering the process employed for the chemical examination, to regard *three* different cases as possible:

I. The arsenious acid is found in the solid state in the contents of the stomach and intestines, or in the vomited matters.

II. The poison is intimately and invisibly mixed with, or dissolved in, the contents, &c., and can therefore no longer be found, or separated by mechanical means, in the solid state.

III. The stomach and intestines are empty, or no arsenic can be detected in them, since it has already been absorbed into the mass of the blood, or into the substance of the different organs.

I. The arsenic is still to be found in the solid state, and may be picked out or separated by levigation from

the contents of the stomach, &c. This case is the easiest of the three since it is only to be proved that the substance found is really arsenic. This may be known by the grains or particles exhibiting the following characters, after having been properly freed from organic matter:

- 1. The particles are generally milk-white, more rarely clear and semi-transparent, hard, and brittle.
- 2. A particle of arsenious acid, however small, when introduced into a small tube closed at one end, and heated in the edge of the spirit-flame, volatilizes and recondenses farther up the tube, in the form of a white sublimate which may be seen, especially when examined with a lens, by sun-light, to consist of very lustrous octohedral crystals.
- 3. A small fragment placed upon red-hot charcoal, is volatilized, emitting a powerful odour of garlic (on red-hot glass or porcelain it volatilizes *without* garlic odour, because it is not reduced to the state of metal).
- 4. A particle of the substance is placed in the end of a very narrow tube, and above it several splinters of freshlyignited charcoal so that they may occupy about ½ inch of the tube. This part of the tube is now held horizontally, in the flame of the spirit-lamp, in such a manner that the spot where the arsenious acid is placed may remain without the flame. When the charcoal is heated to redness, that portion of the tube is also brought into the flame, when the volatilized arsenious acid, passing over the red-hot charcoal, is reduced, and the metallic arsenic deposited beyond the charcoal, in the form of a dark, lustrous, metallic ring. By a gentle heat, this metallic incrustation may be carried still farther up the tube. If the incrustation be chased hither and thither in the tube, it is oxidized, or at least partly, and converted into small shining, colourless, volatile crystals of arsenious

acid. If the tube be cut off, just before the part which contains the metallic ring, and the latter then gently heated, the characteristic garlic odour of arsenic may be perceived on approaching the nose to the orifice of the tube.

- 5. This reduction of arsenic to the metallic state may be effected with greater ease and certainty by dissolving a small quantity of the substance in water containing hydrochloric acid, and testing the solution in Marsh's apparatus, in the manner to be presently described more particularly.
- 6. A particle of the arsenious acid is heated in a small glass tube, closed at one end, with a piece of dry acetate of potassa about as large as a pin's head, when the indescribably offensive and characteristic odour of kakodyl should be evolved.
- 7. One or more fragments are finely powdered, under distilled water, the powder rinsed into a small beakerglass with 20 or 30 drops of water, and the mixture heated nearly to ebullition until the powder is dissolved. A part of this solution is mixed, in a small test-tube, with several drops of solution of nitrate of silver, and afterwards with very dilute ammonia, added drop by drop. In this way, if the substance were arsenious acid, a considerable bright yellow precipitate of arsenite of silver will be produced.—Another portion of the liquid, mixed with several drops of a clear solution of ammonio-sulphate of copper, gives a fine yellowish-green precipitate of arsenite of copper. A third quantity of the solution, mixed with a few drops of hydrochloric acid, and afterwards with several times its volume of sulphuretted-hydrogen-water, gives a bright yellow precipitate of

tersulphide of arsenic, which redissolves perfectly on adding ammonia.

Of all these reactions, the reduction to the metallic state in Nos. 4 and 5 is the most necessary, because it is most characteristic and conclusive. The others are to be viewed rather in the light of superfluous confirmations, and are only employed when a considerable quantity of substance is at the analyst's disposal.

II. Arsenic can no longer be perceived by the eye, or mechanically separated, in the solid state, but is contained in a state of solution, or of intimate mixture, in the contents of the stomach, &c. In this case, which is more difficult and of more frequent occurrence than the preceding, the problem consists in dissolving and destroying, by appropriate reagents, the whole mass of the organic matter composing the contents, the vomited matters, the food, and even the stomach and intestines themselves. This is always necessary before the arsenic can be detected with certainty.

It is indispensably necessary that this operation should be preceded by a most careful examination of the reagents to be employed, in order to ascertain whether they contain, as is not unfrequently the case, a small quantity of arsenic. This is equally requisite whether the reagents have been purchased or have been prepared by the analyst himself. The distilled sulphuric acid, the hydrochloric acid, and the zinc must especially be examined. This is most conveniently effected in Marsh's apparatus, which will be presently described, and which is invaluable as allowing the reagents, which are employed in it, to be so readily and surely tested. Without such previous proof of the absence of arsenic in the reagents, upon which the chemist must

lay great stress in his depositions, the detection of arsenic in investigations of this description cannot be brought forward in evidence, since it might have been derived from the reagents employed. It should farther be observed and stated in evidence, that the investigation was conducted with new utensils and vessels which had not been used before; and it is advisable, moreover, to ensure perfect satisfaction, that it should not be carried out in an ordinary chemical laboratory, or, at all events, that the laboratory should be well cleared before the judicial inquiry is entered upon.

If arsenic should be found in an examination conducted with all these precautions, it is still necessary to reflect that it might occur in the body quite accidentally; especially after the administration of certain medicinal remedies, such as the antimonial compounds, preparations of phosphorous, phosphoric, sulphuric, and hydrochloric acids, which may contain arsenic from carelessness in their preparation. Even the hydrated sesquioxide of iron, administered as an antidote in a suspected case of poisoning, might have contained arsenic, unless prepared with great care. Or the arsenic may have been administered as a remedy (especially as a secret medicine). When bodies have been exhumed, it becomes necessary to test the earth with which the coffin has been in contact, since it sometimes happens that soils, especially such as are ferruginous, contain appreciable quantities of arsenic, which might have entered into the body.

Various methods are employed for the modification or destruction of the organic matters, with a view to the extraction of the arsenic.

1. When the substance is in the form of a paste, as in the contents of the stomach and in the fæces, chlorinegas is passed to saturation. The chlorine is prepared by means of sulphuric acid and manganese, which have been previously tested, and is washed by passing through a small but high column of water. In order to assist the action, the mass may, at the same time, be gently heated. Lastly, when it is completely saturated with gas, coagulated, and bleached, the mixture is heated nearly to ebullition to expel the excess of chlorine, and the solution, which must contain the arsenic, is filtered through paper free from smalt.

- 2. The stomach and intestines, with their contents, are cut into fine shreds, placed in a porcelain dish, and the whole mass uniformly mixed. About \(\frac{1}{3} \) is then set aside in a clean covered glass, in case any accident should happen to the remainder. The mass is then treated with a moderately concentrated solution of potassa, and heat applied until it is entirely or almost entirely dissolved. Only a small quantity of potassa is necessary for this purpose, and the potassa should therefore be gradually added to the mixture, so as to avoid an excess, which would interfere with the subsequent operations. The solution is afterwards slightly acidified with dilute sulphuric acid, and chlorine-gas is passed, to saturation, into the mass thus coagulated, as in 1.
- 3. The organic matter cut into shreds, is treated with about as much pure concentrated hydrochloric acid as is equal to the weight of the dry substances contained in the mass; enough water is then added to form a thin paste. The dish is heated on a water-bath, the contents stirred every five minutes, and about 30 grs. of chlorate of potassa (free from lead) added to the hot liquid until it has become clear yellow, homogeneous, and limpid. After being heated for some time longer, the solution

is strained through a moistened filter of white paper, free from smalt, the residue washed upon the filter with hot water till the washings are no longer acid, the whole liquid poured together into a porcelain dish, and evaporated to about 1 pound upon the water-bath.

The solution obtained by one of these methods is poured into a cylindrical glass or into a flask, and a slow stream of sulphuretted hydrogen gas passed into it to complete saturation. All the arsenic is thus precipitated as sulphide. Its precipitation is much promoted if the liquid be heated for about half an hour to 50° or 60°, while the gas is passing, and allowed to cool before the stream of gas is discontinued. When saturated, the liquid is allowed to remain for twenty-four hours in a closed vessel. The precipitate which is then deposited has generally, even if much arsenic be present, a dirty, undecided, greyish-brown colour.* The greater portion of the solution is poured off, and the precipitate thrown upon the smallest possible filter of Swedish paper, free from smalt, upon which it is well washed. The filtrate, before being thrown away, should, for greater certainty, again be saturated with sulphuretted hydrogen gas and set aside for some time in a closed vessel.

This precipitate always contains, in addition to sulphide of arsenic, certain sulphuretted organic matters which are precipitated with it, and must be completely destroyed; this is best effected in the following manner:

The filter containing the precipitate is placed in a somewhat capacious crucible of genuine porcelain, and digested with concentrated nitric acid until the whole is converted into a homogeneous mass. The free nitric acid, of which

^{*} If lead, copper, mercury, or antimony were present, the precipitate would also contain the sulphides of these metals, for which it would have to be particularly examined.

more may be added if necessary, is neutralized with pure carbonate of soda, and the solution carefully evaporated to dryness. It is important that the mass should contain a sufficient quantity of nitrate of soda, which is easily ensured. It is gradually heated over a large spirit-lamp, or gas-burner, until the salt fuses; it blackens at first, but afterwards fuses, quietly and without deflagration, to a clear colourless liquid. The whole of the organic matter is now burnt, and the arsenic converted into arsenate of soda.

Pure concentrated sulphuric acid is then gradually dropped upon the cooled saline mass in the crucible, and a gentle heat applied, until, after addition of an excess of acid, the nitric and nitrous acids are completely expelled, and the mass is converted into bisulphate of soda. If nitric acid containing hydrochloric acid had been originally employed for the oxidation of the sulphuretted hydrogen precipitate, a loss of arsenic might now result, from its volatilization as chloride of arsenic. The purity, in this respect, of the nitric acid and carbonate of soda, must therefore have been previously ascertained.

The acid saline mass is now dissolved, in the crucible itself, with the smallest quantity of hot water, and the solution introduced into Marsh's apparatus.

4. The organic matter is introduced, together with the whole of the liquid, into a capacious tubulated retort, and about an equal weight of rock-salt, or of fused common salt, in small fragments, added. The retort is connected with a tubulated receiver, furnished with a delivery-tube which dips into water. A quantity of (tested) sulphuric acid, sufficient to decompose the whole of the chloride of sodium, is then poured upon the mass through a funnel tube passed into the tubulure of the retort. When the intumescence and evolution of hydrochloric acid have ceased,

the contents of the retort are heated to boiling, the receiver being kept thoroughly cool. All the arsenic is thus distilled off as chloride, especially towards the last, in proportion as the contents of the retort become more concentrated, on which account the distillation should be carried pretty far. The arsenic is converted into chloride, even when it exists in the mass, in the form of sulphide. The distillate may be at once introduced into Marsh's apparatus. It is safer, since some organic matter might possibly have passed over, to precipitate the arsenic from the solution by sulphuretted hydrogen, and to treat the precipitate as directed above. In the same way the small quantity of arsenic contained in the water in which the hydrochloric acid was condensed, may be precipitated.

Marsh's apparatus has the following simple construc-

tion: a is a

bottle capable of holding $\frac{1}{2}$, or at most 1 pint. Both necks are fitted with new perforated corks, which must be perfectly tight. Through one of these, the funnel-tube δ is passed air-tight, and through the other, the bent tube c, which is expanded at c into a bulb about an inch in diameter. This bulb serves to collect the

particles of liquid which are thrown up from the contents of the bottle, and which drop down again into the latter, from the obliquely cut end of the tube. The other end of this tube is connected, by means of a cork, with the tube d, about 6 inches long, which is filled with fused pure chloride of calcium, free from powder, destined to retain the moisture. In the opposite end of the tube d, is fixed, air-tight, another tube e, made of glass free from lead,

12 inches long, and at most $\frac{1}{12}$ inch in internal diameter. It should be made of rather thick glass, and somewhat drawn out at the end. It must be observed that the funnel-tube d is indispensably necessary. If a two-necked bottle cannot be procured, one with a single neck must be provided with a cork bored with two holes.

Several ounces of granulated zinc are introduced into the bottle, which is then half-filled with distilled water; when the apparatus is all arranged, distilled concentrated sulphuric acid is added in small portions by the funnel tube b, very gradually, so that the mixture may not become too hot, lest sulphuretted hydrogen should be formed. The evolution of hydrogen is allowed to proceed until it is judged that all atmospheric air is expelled, and that the apparatus is perfectly filled with hydrogen.

The narrow delivery-tube is then heated to redness at e, for at least half an hour, by a spirit-lamp with a double draught, or a powerful gas-burner, the evolution of hydrogen being constantly maintained by adding acid from time to time. In this way, the acid and zinc are tested for any trace of arsenic which might be present. If they are pure, no incrustation will be deposited at the ignited spot, e. If arsenic be present, a metallic mirror is obtained at this portion of the tube, and the acid and zinc cannot be used; even the apparatus must then be carefully cleaned, or, better, replaced by a new one. In the same manner any arsenic might be detected in the hydrochloric acid, the chlorate of potassa (after having been completely converted by fusion into chloride of potassium), the nitre, and the hydrate of potassa (for the third case), which must first be converted into sulphate by adding sulphuric acid. The quantities employed for testing should not be too small; at least an ounce of each reagent should be taken.

When the reagents have been tested in this manner, and shown to be absolutely free from arsenic, the examination of the substance may be proceeded with. The solution to be tested, containing any arsenic which may have existed in the body, is poured through the funnel tube b into the apparatus filled with hydrogen, and from which hydrogen is being evolved, the tube e being already heated to redness at the same spot. In order that none of the liquid may remain in the tube b, the latter is rinsed with about the same quantity of pure water, care being taken that no air is poured in with it.

If arsenic be present, there will soon appear, in the portion of the tube e, beyond the heated spot, a dark stain which is at first brownish, and afterwards becomes lustrous and gradually increases until, when large quantities of arsenic are present, it forms an opaque metallic mirror. At the same time, the gas issuing from the tube e may be kindled, and a dish of white genuine porcelain held in the flame, which should not be too feeble; lustrous black or brownish spots of metallic arsenic will then be deposited, and a great many may sometimes be obtained. When the heated portion of the tube is not very long, more or less arsenetted hydrogen escapes decomposition and furnishes the above-mentioned spots. No imitation of porcelain (stone-ware or delf) should be employed for this purpose, since the glaze of these materials very often contains lead, the reduction of which might produce dark spots even though no arsenic were present. If a large quantity of arsenic be contained in the mixture, so that many thick arsenic-spots can be obtained, they may be easily recognized by means of the characteristic reactions given above, after they have been dissolved in a few drops of nitric acid, and the greater excess of acid has been expelled by a very gentle heat. If only traces of arsenic be present, the spots are so feeble that their nature may remain uncertain. The only indication, which is perfectly conclusive is the production, in the red-hot tube, of a metallic mirror, which must volatilize when gently heated, and re-condense upon a cool part of the tube, at the same time imparting to the evolved gas the peculiar garlic odour.

When the arsenical mirror no longer increases, and the flame ceases to deposit the spots, the operation is discontinued. It is then very convenient to draw the tube e gently out, while it is still red-hot and soft, and to close it, when the metallic mirror is obtained in a tube, which may be sealed also at the other end, and laid before the authorities.

If the analyst have reason to believe that a large quantity of arsenic is present, it is well not to employ the whole quantity of liquid at once, but to divide it into several portions, and to make use of a much longer tube e, so as to obtain the arsenic-mirror in several places. The tube is then cut with a file into as many pieces as there are mirrors of arsenic. That which contains the most characteristic mirror is sealed at both ends and produced in court; the remaining mirrors are subjected to the tests given at p. 214, among which the ready volatility and alliaceous odour are the most characteristic and decisive.

If, after heating the tube for one hour, no stain or mirror make its appearance, and no traces of spots have been obtained from the flame, the absence of arsenic may be inferred, provided that proper care have been taken in the former part of the examination, so that the arsenic cannot have been lost through negligence or awkwardness.

It is very important, in connection with this test

(Marsh's) to remember that antimony also, whether as teroxide, or as antimonic acid, and especially when in solution in the form of a salt, yields, under the same conditions as arsenic, a gaseous antimonetted hydrogen, which deposits upon the heated tube, and upon porcelain, a mirror and spots very similar to those obtained with arsenic. This fact assumes so much greater importance, when it is remembered that preparations of antimony, especially tartar emetic, are administered as internal remedies, so that, in such cases, metallic mirrors are obtained, similar to those of arsenic, but consisting, not of that metal, but of antimony. On the other hand, it must not be forgotten that commercial arsenic, as it is employed for poisoning, frequently contains antimony.

If the question be merely whether a metallic mirror consist of arsenic or antimony, it may be readily decided. The arsenic may be easily recognized by the reactions mentioned above, while the antimony-mirror presents very different characters. The antimony-mirror has a lighter colour, and is more lustrous than that of arsenic, the antimony spots are darker and have often a tinge of blue. Antimony is not nearly so easily volatilized as arsenic, and although both mirrors may be chased from one part of the tube to another, there is a great difference in the heat necessary in the two cases. A very striking difference between the two deposits is seen in their behaviour when heated; the mirror of antimony, before volatilizing, fuses into small lustrous globules, which may, in all cases, be seen with the aid of a lens; the arsenic, however, exhibits no sign of fusion. The most characteristic distinction is the production of the garlic odour when the arsenic is volatilized, while the antimony passes off in vapour without any perceptible odour. If that portion of the tube which

contains the mirror be heated while the hydrogen is still passing, the gas issuing from the orifice of the tube will have a distinct garlic odour if the deposit consist of arsenic, but will be inodorous if antimony only be present. The following reactions may also be applied to distinguish arsenic and antimony.

The arsenical spots deposited upon porcelain disappear when moistened with a concentrated alkaline solution of hypochlorite of soda; those of antimony, however, are not affected by this reagent. If the spots consist of arsenic and antimony, the latter not exceeding 5 per cent, the spots will also be entirely dissolved. Spots or mirrors of arsenic disappear when moistened with a drop of nitric acid, and gently warmed, forming a clear solution. If a drop of nitrate of silver be added to the solution, and a glass rod moistened with caustic ammonia be held over the liquid, but not allowed to touch it, the mixture assumes a yellow colour, from the formation of a precipitate of arsenite of silver. Sometimes, if too strong an acid or too great a heat have been applied, the precipitate consists of reddish-brown arsenate of silver. This characteristic colour is always produced by nitrate of silver, when the arsenic spots are dissolved by placing the capsule over a vessel containing solution of chloride of lime and sulphuric acid.

It is true that spots and mirrors of antimony also disappear when treated with nitric acid, the antimony, however, is not dissolved, but merely converted into white oxide, which gives no reaction with solution of nitrate of silver. The antimony dissolves in a mixture of one drop of nitric acid and one drop of hydrochloric acid; if the greater excess of acid be carefully evaporated, and sulphuretted-hydrogen-water be dropt upon the residue,

a fiery-red precipitate of sulphide of antimony is produced. If the spot had consisted of arsenic, a lemon-yellow precipitate would have been obtained.

If the spots be moistened with sulphide of ammonium, and dried at a very gentle heat, the arsenic becomes yellow the antimony orange. The yellow spots of sulphide of arsenic are not affected by hydrochloric acid, while those of sulphide of antimony disappear on gently heating.

If sulphuretted hydrogen gas be passed through the tube containing the metallic mirror, and heat applied, the metal is converted into a sulphide. If the mirror consist of antimony, black, or partly orange-red, sulphide of antimony is produced, while arsenic gives a yellow sulphide. The colour, however, is not the only distinction between these compounds, another is afforded by their unequal volatility, sulphide of arsenic being far more volatile than that of antimony.

Moreover, antimony and arsenic, in the form of sulphides, may be separated by cyanide of potassium, according to the method given in No. 55.

The presence of antimony in the precipitated sulphides may also be ascertained by oxidizing them as directed at p. 220. In that case, the fused mass, before treatment with sulphuric acid, should be dissolved in water, when the antimony would remain undissolved in the form of antimonate of soda.

III. If no arsenic have been found in the stomach and intestines, it must be supposed to have been partly carried away in the vomited matters and fæces, and partly absorbed into the mass of the blood, and into those organs which are rich in blood. In this case, the same process is employed as in the preceding, the arsenic being sought, according to the same method, in the liver, spleen, lungs,

heart, and kidneys. If urine were found in the bladder, or fæcal matter in the large intestines, they should be examined first. The urine must not be introduced at once into Marsh's apparatus, since the frothing to which it gives rise would interfere with the progress of the experiment; the urine should therefore be slightly acidified, with hydrochloric acid, sulphuretted hydrogen passed through it, and the subsequent process conducted as in the second case.

Investigations of this description are in the highest degree laborious, troublesome, and disgusting, when the body to be examined has been interred for months or years, and has passed into a state of putrefaction. In such a case, it is frequently no longer possible to distinguish or separate individual organs, and the analyst is then necessitated to examine the whole mass of putrified organs, or the whole of the soft parts which dry up under some particular local circumstances, and even the bones. When this is the case, the body should not be laid in a bath of chlorine-water or solution of chloride of lime, in order to destroy the offensive odour, since arsenic may thereby be extracted and lost. If chlorine-gas be employed to disinfect the body, it must be evolved by means of distilled sulphuric acid free from arsenic. All the soft parts, especially those which may have formed parts of the abdominal viscera, are carefully separated from the bones, and treated as in the second case

The following is another convenient process to be especially preferred for the treatment of bodies which have been exhumed entire after some months interment.

The entire soft parts are treated in a large dish of genuine porcelain, with moderately strong nitric acid, which has been previously tested for arsenic; the dish is

10

then heated upon a sand-bath, and its contents well stirred, until the organic matters are so far destroyed and dissolved as to form a homogeneous pasty mixture. This is now neutralized with a solution of pure hydrate or carbonate of potassa, and about as much finely-powdered nitre (previously tested) added, as is equal in weight to the soft parts. The whole is now evaporated to dryness, with constant stirring, and the dry mass introduced by degrees, in small portions, into a new clean Hessian crucible heated to dull redness. In this manner, the whole of the organic matter is burnt, and the arsenic, if present, converted into arsenate of potassa. In this process, it is important, and not very easy, to add the proper quantity of nitre. If too little nitre be employed, part of the organic matter may remain unburnt, and arsenic may be volatilized from the carbonaceous mass; on the other hand, too much nitre would interfere with the subsequent treatment of the mass. It is better to make a preliminary test with a small portion of the mixture, by introducing it into a small red-hot crucible, and observing whether the mass is perfectly white after deflagration. If it be black and carbonaceous, more nitre must be added.

The mass, which now consists essentially of carbonate, nitrate, and nitrite of potassa, and may also contain arsenate of potassa, is dissolved in the smallest possible quantity of boiling water, and the solution, without filtering off from the suspended phosphate of lime and silica, gradually mixed, in a porcelain dish, with a slight excess of sulphuric acid. The pasty saline mass thus produced is carefully heated till all the nitrous and nitric acids are expelled, a point to which great attention must be paid. On cooling, the mass is stirred up with a little cold water, and the solution poured off from the large deposit of sul-

phate of potassa. The latter is washed several times with cold water, the washings mixed with the first solution, and the liquid, treated as above, with sulphuretted hydrogen. The precipitate then only requires to be oxidized with nitric acid, with the precaution that the acid must be entirely removed by evaporation before the solution is introduced into Marsh's apparatus.

It is rarely of importance to the evidence that the weight of arsenic existing in a body should be determined. Such an estimation can only be relative, since it is impossible to extract and weigh the whole of the arsenic contained in all the parts of a body. In such a case, a somewhat longer reduction-tube should be employed, into which is introduced a closely twisted spiral of pure bright copper, about two inches in length; this spiral is accurately weighed with the tube. The latter is then heated in two places, one nearer the evolution-bottle, for the deposition of a mirror; the other, at some distance, where the strip of copper is placed, which combines with all the remaining arsenic, forming steel-grey arsenide of copper. The increase of weight of the tube indicates the amount of arsenic, which is calculated as arsenious acid.

EQUIVALENT WEIGHTS OF THE ELEMENTS.

		O=100.	H=1.
Aluminum	Al	342.5	27.4
Antimony	Sb	1612.5	129
Arsenic	As	937.5	75
Barium	Ba	856.25	68.5
Beryllium	Be	176.25	14.1
Bismuth	Bi	2600	208
Boron	В	136.25	10.9
Bromine	Br	1000	80
Cadmium	Cd	700	56
Calcium	Ca	250	20
Carbon	C	75	6
Cerium	Ce	587.5	47
Chlorine	Cl	443.75	35.5
Chromium	Cr	333.75	26.7
Cobalt	Co	368.75	29.5
Copper	Cu	396.25	31.7
Didymium	D	625	50
Erbium	E		58
Fluorine	F	237.5	19
Gold	Au	2462.5	197
Hydrogen	H	12.5	1
Iodine	I	1588.75	127.1
Iridium	Ir	1237.50	99
Iron	Fe	350	28
Lanthanium	La	587.5	47
Lead	Pb	1296.25	103.7

		O=100.	H=1.
Lithium	Li	81.25	6.5
Magnesium	Mg	150	12
Manganese	Mn	345	27.6
Mercury	Hg	1250	100
Molybdenum	Mo	575	46
Nickel	Ni	370	29.6
Niobium	Nb		
Nitrogen	N	175	14
Norium	No		
Osmium	Os	1245	99.6
Oxygen	0	100	8
Palladium	Pd	666.25	53.3
Pelopium	Pe	Jan Britan	
Phosphorus	Ρ.	387.5	31
Platinum	Pt	1233.75	98.7
Potassium	K	490	39.2
Rhodium	R	652.5	52.5
Ruthenium	Ru	652.5	52.5
Selenium	Se	493.75	39.5
Silicium	Si	266.25	21.3
Silver	Ag	1351.25	108.1
Sodium	Na	287.5	23
Strontium	Sr	547.5	43.8
Sulphur	S	200	16
Tantalum	Ta .	2300	184
Tellurium	Te .	802.5	64.2
Terbium	Tb .		Transfer
Thorium	Th .	745	59.6
Tin	Sn	725	58
Titanium	Ti .	312.5	25
Tungsten	W	1150	92
Uranium	U.	750	60
Vanadium	V	857.5	68.6
Yttrium	Y		patratist.
Zine	Zn .	407.5	32.6
Zirconium	Zr .	840	67:2

EQUIVALENT WEIGHTS OF COMPOUND BODIES.

0 = 100.

Alumina			0 = 100.	H=1.
Alumina		(KO, SO, AloOn)		
Alumina	Alum	3SO ₂ + 24HO	5932.5	502
—— carbonate of . 2NH₄O, 3CO₂ 1475 118 Ammonium . . NH₄Cl 668·75 53·5 —— chloride of . . NH₄Cl 668·75 53·5 —— platinochloride of . . NH₄Cl, PtCl₂ 2790 223·2 Arsenate of magnesia-ammonia . Asso₃ 1912·5 153 Arsenious acid . . AsO₃ 1237·5 190 Baryta . . BaCl 1300 104 Baryta . . BaO, CO₂ 1231·25 98·5 —— carbonate of . BaO, CO₂ 1231·25 98·5 Baryta . . BaO, CrO₃ 1590 127·2 Berylla (glucina) Be₂O₃ 476·25 52·2 <	Alumina		642.5	78.8
—— carbonate of . 2NH₄O, 3CO₂ 1475 118 Ammonium . . NH₄Cl 668·75 53·5 —— chloride of . . NH₄Cl 668·75 53·5 —— platinochloride of . . NH₄Cl, PtCl₂ 2790 223·2 Arsenate of magnesia-ammonia . Asso₃ 1912·5 153 Arsenious acid . . AsO₃ 1237·5 190 Baryta . . BaCl 1300 104 Baryta . . BaO, CO₂ 1231·25 98·5 —— carbonate of . BaO, CO₂ 1231·25 98·5 Baryta . . BaO, CrO₃ 1590 127·2 Berylla (glucina) Be₂O₃ 476·25 52·2 <			212.5	17
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			1475	118
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			225	18
NH4Cl, PtCl2 2790 223·2		NH ₄ Čl	668.75	53.5
Antimonious acid				
Arsenate of magnesia-ammonia Arsenic acid				
Arsenic acid				153
Arsenious acid				
Barium, chloride of				
Saryta				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
— chromate of				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
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Bismuth, teroxide of . . $\mathring{BiO_3}$ 2900 232 Bitartrate of potassa . . KO, HO T 2352·5 188·2 Cadmium, oxide of . . CdO 800 64 Calcium, chloride of . . CaCl 693·75 55·5 Carbonic acid . . CO $_2$ 275 22 Chromate of lead . . CrO $_3$ 633·75 50·7 Chromium, sesquioxide of . . CrO $_3$ 967·50 77·4 Cobalt, protoxide of . . CuO 468·75 37·7 Copper, protoxide of . . CuO 496·25 39·7 Cyanide of silver . . AgCy 1676·25 134·1 Cyanogen . . . 2KCy, FeCy = K_2Cfy 2305 184·4 . . . 2KCy, FeCy + 3 HO) 20.0 11.4				
Bitartrate of potassa KO, HO T 2352·5 188·2				
Cadmium, oxide of CdO 800 64 Calcium, chloride of CaCl 693·75 55·5 Carbonic acid CC2 275 22 Chromate of lead PbO, CrO3 2030 162·4 Chromic acid CrO3 633·75 50·7 Chromium, sesquioxide of Cr203 967·50 77·4 Cobalt, protoxide of CoO 468·75 37·5 Copper, protoxide of Cu0 496·25 39·7 Cyanide of silver Cu20 892·5 71·4 AgCy 1676·25 134·1 Cyanogen 2KCy, FeCy = K2Cfy 2305 18·4 " " Contain- 2KCy, FeCy + 3 HO 10.40-2.2 211.44				
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Suboxide of				The second second
Cyanide of silver				
Cyanogen $C_2N = Cy$ 325 26 Ferrocyanide of potassium $2KCy$, $FeCy = K_2Cfy$ 2305 184.4				All of the latest and
Ferrocyanide of potassium . 2KCy, FeCy = K ₂ Cfy 2305 184'4				
" " contain- (2KCy, FeCy + 3 HO)			90014	
			2305	184.4
			2642.5	211.4

		0 = 100.	H=1.
Fluoride of calcium	CaF	487.5	39
Hydrochloric acid	HCl	556.25	36.5
Iodide of palladium	PdI	2255	180.4
—— of potassium	KI	2078.75	166.3
Iron, protoxide of	FeO	450	36
—— sesquioxide of	Fe ₂ O ₃	1000	80
Lead, acetate of	PbO, A + 3HO	2371.25	189.7
—— chloride of	PbCl	1740	139.2
—— protoxide of	PbO	1396.25	111.7
red oxide of	PbO, Pb ₂ O ₃	4288.75	343.1
Lime	CaO	350	28
— carbonate of	CaO, CO,	625	50
Magnesia	MgO	250	20
Manganese, peroxide of	MnO ₂	545	43.6
protosesquioxide of .	MnO, Mn ₂ O ₃	1435	114.8
protoxide of	MnO	445	35.6
Mercury, protochloride of	HgCl	1693.75	135 5
—— protoxide of	HgO	1350	108
subchloride of	Hg _o Cl	2943.75	235.5
suboxide of	Hg ₂ O	2600	208
Molybdenum, binoxide of	MoO ₂	775	62
Molybdic acid	MoO ₃	875	70
Nickel, protoxide of	NiO	470	37.6
Nitrate of baryta	BaO, NO ₅	1631.25	130.5
lead	PbO, NO ₅	2071.25	165.7
——— potassa	KO, NO ₅	1265	101.2
silver	AgO, NO ₅	2126-25	170.1
——— soda	NaO, NO	1062.5	85
strontia	SrO, NO	1322.5	105.8
Nitric acid	NO ₅	675	54
hydrated	HO, NO ₅	787.5	63
Oxalic acid	C_2O_3	450	36
hydrated	$3HO, C_2O_3$	787.5	63
*Phosphate of magnesia	2MgO, PO ₅	1387.5	111
b — soda	2NaO, PO ₅	1662.5	133
b soda with water of			
crystallization	$2NaO, HO, PO_5 + 24HO$	4475	358
Phosphoric acid	PO_5	887.5	71
Potassa	КО	590	47.2
bichromate of	KO, 2CrO ₃	1857.5	148.6
carbonate of	KO, CO ₂	865	69.2
chlorate of	KO, ClO ₅	1534.75	122.7
chromate of	KO, CrO ₃	1223.75	97.9
hydrate of	ко, но	702.5	56.2
Potassium, chloride of	KCl	933.75	74.7
platino-chloride of .	KCl, PtCl ₂	3055	244.4
Silicic acid	SiO ₃	566.25	45.3
Silicon, terfluoride of	SiF ₃	987.75	78.3
Silver, chloride of	AgCl	1795	143.6

		1	
		0-100.	H=1.
Silver, oxide of	AgO	1451-25	1 6.1
Soda	NaO	387.5	31
Soda, carbonate of	NaO, CO ₂	662.5	53
of crystallization	NaO, $CO_2 + 10HO$	1787.5	143
— hydrate of	NaO, HO	500	40
Sodium, chloride of	NaCl	731.25	58.5
Stannic acid	SnO ₂	925	74
Strontia	SrO	647.5	51.8
Sulphate of ammonia	NH_4O , $SO_3 + HO$	937.5	75
baryta	BaO, SO ₃	1456.25	116.5
copper	$CuO, SO_3 + 5HO$	1558.75	124.7
lead	PbO, SO ₃	1896.25	151.7
lime	CaO, SO ₃	850	68
potassa	KO, SO_3	1090	87.2
protoxide of iron .	FeO, $SO_3 + 7HO$	1737.5	139
soda	NaO, SO ₃	887.5	71
strontia	SrO, SO ₃	1147.5	91.8
Sulphide of antimony	SbS_3	2212.5	177
arsenic	AsS ₃	1537.5	123
copper	CuS	992.5	47.7
lead	PbS	1496.25	119.7
mercury	HgS	1450	116.0
molybdenum	MoS_2	975.5	78.0
silver	AgS	1551-25	124.1
zinc	ZnS	607.5	48.6
Sulphuretted hydrogen	HS	212.5	17
Sulphuric acid	SO_3	500 .	40
hydrated	HO, SO ₃	612.5	49
Sulphurous acid	SO ₂	400	32
Tin, protoxide of	SnŌ	825	66
Titanic acid	TiO ₂	512.5	41
Tungstic acid	WO_3	1450	116
Water	но	112.5	9
	2HO	225	18
	3НО	337.5	27
	4HO	450	36
	5HO	562.5	45
	6НО	675	54
A PROPERTY OF THE PERSONS ASSESSMENT	7HO	787.5	63
	8H0	900	72
The state of the s	9HO	1012.5	81
The state of the s	10HO	1125	90
Zinc, oxide of	ZnO	507.5	40.6

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ADDENDA.

(1) Purification of Tellurium.—Tellurium may be readily distilled from a little porcelain retort, which is placed in an ordinary small wind-furnace, without a current of hydrogen being necessary.

Crude tellurium, containing lead, may now be had for £1 at Vienna. See foot-note to p. 100.

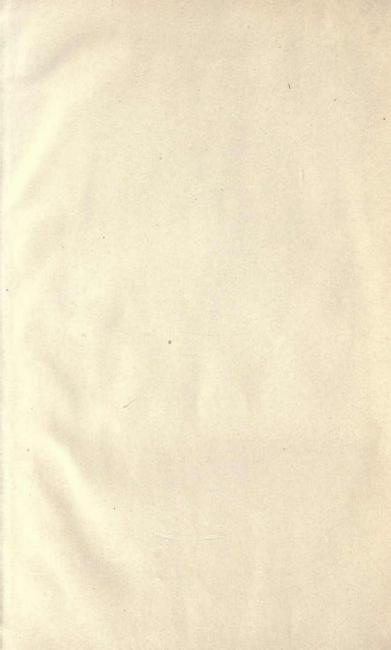
(2) SEPARATION OF NICKEL FROM ZINC.—A better method of separating zinc and nickel consists in mixing the solution, previously much concentrated by evaporation, with excess of hydrate of potassa, and afterwards with hydrocyanic acid, so that the two oxides may be entirely dissolved as double cyanides. From this solution the zinc is entirely precipitated, as sulphide of zinc, by protosulphide of potassium (not sulphide of ammonium), while the nickel remains in solution. The filtered liquid is then boiled with aqua-regia, and the oxide of nickel precipitated by hydrate of potassa.

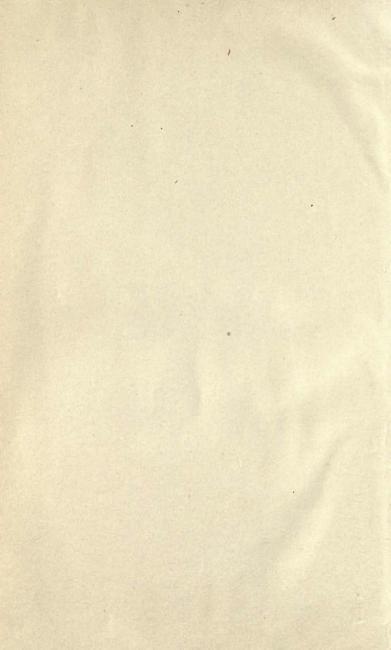
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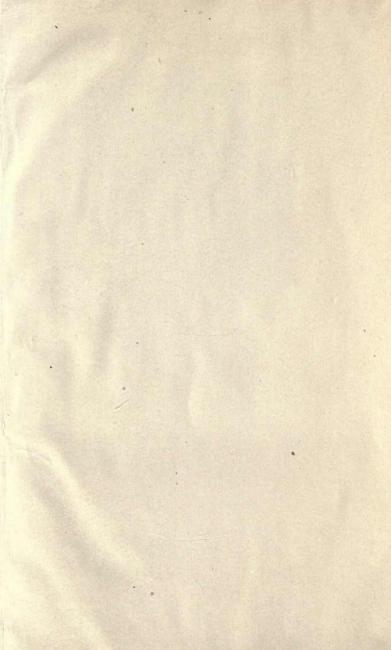
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